METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY--DETERMINATION OF PESTICIDES IN WATER BY C-18 SOLID-PHASE EXTRACTION AND CAPILLARY-COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY WITH SELECTED-ION MONITORING

U.S. GEOLOGICAL SURVEY

Open-File Report 95-181

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By Steven D. Zaugg, Mark W. Sandstrom, Steven G. Smith, and Kevin M. Fehlberg

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U.S. Geological Survey

Open-File Report 95-181

Denver, Colorado
1995

U.S. DEPARTMENT OF THE INTERIOR

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U. S. GEOLOGICAL SURVEY

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
centimeter (cm)	3.94×10^{-1}	inch
gram (g)	3.52×10^{-2}	ounce
kilogram (kg)	3.53×10^{-1}	ounce, avoirdupois
kilopascal (kPa)	1.45×10^{-1}	pounds per square inch
liter (L)	2.64×10^{-1}	gallon
meter (m)	3.28×10^{0}	foot
microliter (µL)	2.64×10^{-7}	gallon
micrometer (µm)	3.94×10^{-5}	inch
milligram (mg)	3.53×10^{-5}	ounce
milliliter (mL)	2.64×10^{-4}	gallon
milliliter per minute (mL/min)	3.38×10^{-2}	ounce per minute
millimeter (mm)	3.94×10^{-2}	inch
nanogram (ng)	3.53×10^{-11}	ounce

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$°F = 9/5\ (°C) + 32.$$

The following abbreviations are used in this report:

dc	direct current	ng/µL	nanogram per microliter
µg/L	microgram per liter	lb/in^2	pound per square inch
min	minute	V	volt
ng/L	nanogram per liter		

The following terms are used in this report:

C-18	octadecyl	PFA	perfluoralkoxy
EDOC	electronic documents system	PFTBA	perfluorotributylamine
ETFE	ethylenetetrafluoroethylene	SIM	selected-ion monitoring
GC	gas chromatography	SPE	solid-phase extraction
GCC	glass bottle, amber	USGS	U.S. Geological Survey
GC/MS	gas chromatograph/mass spectrometer		
HIP	hexane-isopropanol		
HPLC	high-performance liquid chromatography		
ID	inside diameter		
MDL	method detection limit		
NAWQA	National Water-Quality Assessment program		
NWQL	National Water Quality Laboratory		
OD	outside diameter		
PAH	polyaromatic hydrocarbon		

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BY STEVEN D. ZAUGG, MARK W. SANDSTROM, STEVEN G. SMITH, AND KEVIN M. FEHLBERG

ABSTRACT

A method for the isolation and analysis of 41 pesticides and pesticide metabolites in natural-water samples is described. The pesticides are isolated by C-18 solid-phase extraction and determined by capillary-column gas chromatography/mass spectrometry with selected-ion monitoring. Water samples are filtered to remove suspended particulate matter and then are pumped through disposable solid-phase extraction columns containing octadecyl-bonded porous silica to extract the pesticides. The columns are dried using carbon dioxide or nitrogen gas, and adsorbed pesticides are removed from the columns by elution with hexane-isopropanol (3:1). Extracted pesticides are determined by capillary-column gas chromatography/mass spectrometry with selected-ion monitoring of three characteristic ions. The upper concentration limit is 4 micrograms per liter (µg/L) for most pesticides, with the exception of widely used corn herbicides--atrazine, alachlor, cyanazine, and metolachlor--which have upper concentration limits of 20 µg/L. Single-operator method detection limits in reagent-water samples range from 0.001 to 0.018 µg/L. Recoveries in reagent-water samples ranged from 37 to 126 percent for most pesticides. The estimated holding time for pesticides after extraction on the solid-phase extraction columns was 7 days. An optional on-site extraction procedure allows for samples to be collected and processed at remote sites where it is difficult to ship samples to the laboratory within the recommended pre-extraction holding time.

INTRODUCTION

Pesticides are widely used in the United States to increase production of agricultural products by controlling weeds, insects, and other pests in a wide variety of settings (Gianessi and others, 1986). They are frequently detected in surface water and ground water in the United States (Hallberg, 1989) and Europe (Leistra and Boesten, 1989). The traditional methods for determining residues of pesticides in natural-water samples involve liquid-liquid

extraction with an organic solvent followed by analysis by gas chromatography (GC) with nitrogen-phosphorus or electron-capture detection, using two columns to confirm pesticide identity.

Recently, methods for pesticide analysis using solid-phase extraction (SPE) as an alternative to liquid-liquid extraction have been described (Bagnati and others, 1988; Bellar and Budde, 1988; Eichelberger and others, 1988; Junk and Richard, 1988; Battista and others, 1989; Brooks and others 1989; DiCorcia and others, 1989; Sandstrom, 1989; Thurman and others, 1990). These SPE methods are attractive because they are rapid, efficient, use less solvents than liquid-liquid extraction, and consequently have lower laboratory expenses. The SPE methods can be conducted onsite, which enables processing of samples with labile compounds, or at remote sites. In addition, the SPE methods can be automated by using laboratory robotic systems that do all or part of the sample-preparation steps. Some of these SPE methods also incorporate the use of a gas chromatograph/mass spectrometer (GC/MS) operated under a selected-ion monitoring (SIM) mode for confirmation and quantitation of pesticides. The GC/MS SIM is more specific than either the nitrogen-phosphorus or electron-capture detector, and more sensitive than the nitrogen-phosphorus detector.

This report describes a method for determining a broad range of pesticides in natural-water samples. It was developed by the U.S. Geological Survey (USGS) for use in the USGS National Water Quality Laboratory. The method combines octadecyl (C-18) SPE for pesticide isolation and GC/MS operated in the SIM mode for selective confirmation and quantitation of the pesticides. It is rapid, more efficient, and can detect lower concentration levels (in nanograms per liter) compared to other USGS methods (Wershaw and others, 1987). The method supplements other methods of the USGS for determination of organic substances in water that are described by Wershaw and others (1987) and by Fishman (1993). The method was implemented in the National Water Quality Laboratory (NWQL) in October 1992.

This report provides a detailed description of all aspects of the method, including the equipment, reagents, sampling protocol, instrument calibration, and SPE procedure required for sample analysis. Method performance (precision and accuracy) and estimated method detection limits for 47 pesticides are presented.

The scope of the report includes determination of method performance in ultrapure water samples and two natural-water types--a ground water and a surface water from the Denver, Colorado, region. Method performance was determined at two concentration levels--0.1 and 1.0 µg/L--in each water type. Method detection limits were determined according to an accepted statistical procedure (U.S. Environmental Protection Agency, 1992). Holding times of SPE columns before extraction and the use of an automated evaporation

system for solvent reduction also were evaluated. An optional on-site SPE procedure is described, and an optional laboratory automated procedure is briefly described in Supplements A and B to the report. The method was tested on surface-water samples from the midcontinent of the United States in 1991. During 1992, four study units of the National Water-Quality Assessment (NAWQA) program tested the on-site isolation procedure.

ANALYTICAL METHOD

Organic Compounds and Parameter Codes: Pesticides, dissolved, gas chromatography/mass spectrometry, O-1126-95 (see table 1)

1. Scope and application

This method is suitable for the determination of low-level concentrations (in micrograms per liter and nanograms per liter) of pesticides and pesticide metabolites in natural-water samples. The method is applicable to pesticides and metabolites that are (1) efficiently partitioned from the water phase onto an octadecyl (C-18) organic phase that is chemically bonded to a solid inorganic matrix, and (2) sufficiently volatile and thermally stable for gas chromatography. Suspended particulate matter is removed from the samples by filtration, so this method is suitable only for dissolved-phase pesticides and metabolites.

The compounds include some of those in the NWQL Laboratory Services Catalog (Timme, 1994), as well as newer pesticides determined to be of national importance for the NAWQA program (table 1). The method was developed in response to the request for a broad spectrum pesticide method for use in determining their occurrence and distribution as monitored by the NAWQA program. Pesticides were selected initially because of their widespread use in the United States, according to information in Resources for the Future database (Gianessi and Puffer, 1990, 1992a, and 1992b) and compatibility with the general analytical plan. Other criteria included published studies of pesticide fate and occurrence of metabolites, responses from NAWQA Study Unit personnel regarding pesticides of local significance, and U.S. Environmental Protection Agency health advisories. Finally, restrictions in the analytical software on the number of ions scanned for specific time intervals limited the number of pesticides chosen for testing in the method to about 50.

Table 1.--*Compound name, use, pesticide class, codes,and registry numbers*

[NWQL, National Water Quality Laboratory; CAS, Chemical Abstract Service; MW, molecular weight; USE, annual national use of active ingredient (a.i.) in thousand kilograms (kg) (a.i./1,000 kg, Gianessi and Puffer, 1990, 1992a, 1992b); H, herbicide; AMID, Cl-acetamide; TRI, triazine; --, metabolite or pesticide no longer registered for use; MET, metabolite; I, insecticide; OP, organophosphate; DNA, dinitroaniline; CB, carbamate; OC, organochlorine; UREA, phenyl urea; PYR, permethrin; MISC, miscellaneous; URAC, uracil]

Compound (common chemical name)	Use	Class	NWQL code	Para-meter code	CAS registry number	MW	USE (a.i/ 1,000 kg)
Alachlor (Lasso)	H	AMID	4001	46342	15972-60-8	269.8	25,055
Atrazine	H	TRI	4003	39632	1912-24-9	215.7	29,163
Atrazine, desethyl-[1]	--	MET	4002	04040	6190-65-4	152.1	--
Azimphos-methyl (guthion)[1]	I	OP	4004	82686	86-50-0	317.1	1,125
Benfluralin (Benefin)	H	DNA	4005	82673	1861-40-1	335.3	560
Butylate (Genate Plus, Suntan +)	H	CB	4006	04028	2008-41-5	217.4	8,675
Carbaryl (Sevin)[1]	I	CB	4007	82680	63-25-2	201.2	44
Carbofuran (Furandan)[1]	I	CB	4008	82674	1563-66-2	236.3	1,459
Chlorpyrifos	I	OP	4009	38933	2921-88-2	350.6	7,593
Cyanazine	H	TRI	4010	04041	21725-46-2	240.7	10,394
Dacthal (DCPA, chlorthal-dimethyl)	H	OC	4011	82682	1861-32-1	332.0	1,007
DDE, *p,p'*-	I	OC	4012	34653	72-55-9	318.0	--
Diazinon	I	OP	4013	39572	333-41-5	304.3	776
Dieldrin	I	OC	4015	39381	60-57-1	380.9	--
Diethylanaline, 2,6-	--	MET	4016	82660	579-66-8	149.2	--
Dimethoate[2]	I	OP	4017	82662	60-51-5	229.3	1,344
Disulfoton	I	OP	4018	82677	298-04-4	274.4	1,388
EPTC (Eptam)	H	CB	4019	82668	759-94-4	189.3	16,885
Ethalfluralin (Sonalan)	H	DNA	4020	82663	55283-68-6	333.3	1,597
Ethoprop (Mocap, ethoprophos)	I	OP	4021	82672	13194-48-4	242.3	743
Fonofos (Dyfonate)	I	OP	4022	04095	944-22-9	246.3	1,834
HCH, *alpha*-	I	OC	4023	34253	319-84-6	290.8	--
HCH, *gamma*- (Lindane)	I	OC	4025	39341	58-89-9	290.9	30
Linuron (Lorox, Linex)	H	UREA	4026	82666	330-55-2	249.1	1,191
Malathion	I	OP	4027	39532	121-75-5	330.3	1,447
Metolachlor (Dual)	H	AMID	4029	39415	51218-45-2	283.8	22,570
Metribuzin (Lexone, Sencor)	H	TRI	4030	82630	21087-64-9	214.3	2,189
Molinate (Ordram)	H	CB	4031	82671	2212-67-1	187.3	2,001
Napropamide (Devrinol)	H	AMID	4032	82684	15299-99-7	271.4	317
Parathion	I	OP	4033	39542	56-38-2	291.3	1,293
Parathion, methyl- (Penncap-M)	I	OP	4028	82667	298-00-0	263.2	3,692
Pebulate (Tillam)	H	CB	4034	82669	1114-71-2	203.3	296
Pendimethilan	H	DNA	4035	82683	40487-42-1	281.3	5,685
Permethrin, *cis*-	I	PYR	4036	82687	54774-45-7	391.3	509
Phorate (Thimet)	I	OP	4037	82664	298-02-2	260.4	2,171
Prometon	H	TRI	4039	04037	1610-18-0	225.3	--
Pronamide (Kerb) (Propyzamid)	H	AMID	4038	82676	23950-58-5	256.1	113
Propachlor (Ramrod)	H	AMID	4040	04024	1918-16-7	211.7	1,811
Propanil (Stampede)	H	AMID	4041	82679	709-98-8	218.1	3,412
Propargite (Omite) (alkyl sulfite)	I	MISC	4042	82685	2312-35-8	350.5	1,719
Simazine (Aquazine, Princep)	H	TRI	4043	04035	122-34-9	201.7	1,800
Tebuthiuron (Spike)	H	UREA	4045	82670	34014-18-1	228.3	276
Terbacil (Sinbar)[1]	H	URAC	4046	82665	5902-51-2	216.7	175,
Terbufos (Counter)	I	OP	4047	82675	13071-79-9	288.4	3,277
Thiobencarb (Bolero)	H	CB	4044	82681	28249-77-6	257.8	617
Triallate (Avadex BW, Far-Go)	H	CB	4049	82678	2303-17-5	304.7	1,593
Trifluralin (Treflan)	H	DNA	4050	82661	1582-09-8	335.5	12,312

[1]These pesticides are qualitatively identified and reported with an E code (estimated value) because of problems with gas chromatography or extraction.

[2]Pesticide shows small and variable recovery because of incomplete extraction. This pesticide was deleted from the method in June 1994.

The calibration range is equivalent to concentrations from 0.001 to 4.0 µg/L for most pesticides. Widely and abundantly used corn herbicides--atrazine, metolachlor, cyanazine, and alachlor--have upper concentration limits of 20 µg/L. Method detection limit (MDL) is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99-percent confidence that the compound concentration is greater than zero (Wershaw and others, 1987). The MDL is compound dependent and dependent on sample matrix and instrument performance and other operational sources of variation. For the listed pesticides, MDLs vary from 0.001 to 0.018 µg/L. Analytical results are not censored at the MDL; if a pesticide meets the detection criteria (retention time and mass spectra compared to that of a reference standard, as defined in section 11.1), the result is calculated and reported.

2. Summary of method

2.1 The samples are filtered at the collection site using glass-fiber filters with 0.7-µm pore diameter to remove suspended particulate matter. The procedure for filtration of samples for organic analysis is described by Sandstrom (1995). Filtered water samples are pumped through disposable, polypropylene SPE columns containing porous silica coated with an octadecyl (C-18) phase that is chemically bonded to the surface of the silica. The SPE columns are dried using a gentle stream of carbon dioxide or nitrogen to remove residual water. The adsorbed pesticides and metabolites then are removed from the SPE columns by elution with hexane-isopropanol (3:1). The eluant is further evaporated using a gentle stream of nitrogen. Extracts of the eluant are analyzed by a capillary-column GC/MS operated in the SIM mode.

3. Interferences

Organic compounds having gas-chromatographic retention times and characteristic ions with a mass identical to those of the pesticides and metabolites of interest may interfere.

4. Apparatus and instrumentation

4.1 *Cleaning and elution module for SPE columns*; Supelco, Inc., Visiprep Solid Phase Extraction Vacuum Manifold and Visidry Drying Attachment or equivalent.

4.2 *SPE pump, ceramic-piston, valveless pump*, capable of pumping 0 to 30 mL/min, with fittings for 3.18-mm outside diameter (OD) tubing; Fluid

Metering Inc., Model QSY - 2 CKC or equivalent. For on-site SPE, an SPE pump powered by a 12-V dc motor is needed; Fluid Metering Inc., Model RHB - 0 CKC or equivalent.

4.3 *Teflon-perfluoralkoxy (PFA) tubing*, 3.18-mm OD; Cole-Parmer Instrument Co., CL-06375-01 or equivalent.

4.4 *Tefzel-ethylenetetrafluoroethylene (Tefzel-ETFE) female Luer connector* with 1/4-28 thread, Tefzel-ETFE union with 1/4-28 thread, and Tefzel-ETFE nut with 1/4-28 thread and 3.18-mm OD tubing connector; Upchurch Scientific or equivalent.

4.5 *Pump control box* (optional) for 12-V dc pumps, fitted with a 4-amp fuse, toggle switch, and 10-ohm 1.58-amp variable resistor.

4.6 *Sample-preparation workstation* (optional) for cleaning SPE column; Zymark Inc., Benchmate Workstation or equivalent.

4.7 *Bottle-top solvent dispenser*, adjustable from 2 to 10 mL; Brinkman Dispensette, Van Waters & Rogers (VWR) Scientific or equivalent.

4.8 *Luer stopcocks* (optional), flow control valves or on-off valves, constructed of inert materials; Burdick & Jackson (B&J) Inert PTFE flow control valve, Baxter Diagnostics, Inc. or equivalent.

4.9 *Vacuum pump*--Any vacuum pump with sufficient capacity to maintain a slight vacuum of 1.5 to 3 kPa in the cleaning/elution module.

4.10 *Micropipets*--50- and 100-µL, fixed- and variable-volume micropipets with disposable glass capillaries; VWR Scientific or equivalent.

4.11 *Analytical balances*--Capable of accurately weighing 1,200 g ±1 g and 10.000 g ±0.001 mg. An optional procedure for weighing the SPE columns requires a balance capable of accurately weighing 10.000 g ±0.001 g.

4.12 *Fused-silica capillary column* that provides adequate resolution, capacity, accuracy, and precision. A 25-m x 0.20-mm inside diameter (ID) fused-silica capillary column coated with a 0.33-µm bonded film of polyphenylmethylsilicone was used; Hewlett-Packard Ultra II or equivalent.

4.13 *Automated solvent evaporator*--The heat-bath temperature needs to be maintained at 25°C, and the nitrogen gas pressure at 27.5 kPa (4 lb/in^2); Zymark Inc., TurboVap LV or equivalent.

4.14 *GC/MS bench-top system*; Hewlett-Packard, Model 5971 or equivalent.

4.14.1 GC conditions: Oven, 100°C (hold 5 minutes), then program to 300°C at 6°C/min, then hold for 5 minutes; injection port, 250°C; carrier gas, helium; injection volume, 2 µL, splitless injection.

4.14.2 MS conditions: Interface, 290°C; source, 200°C; analyzer, 100°C; dwell time 20 milliseconds; mass ions monitored are listed in table 2 (see section 9, Calibration).

4.14.3 The apparatus and equipment required for the automated SPE method are listed below; specific sources and models used during the development of this method also are listed, where applicable:

4.14.3.1 *AutoTrace SPE Workstation* configured for 3-mL SPE columns; Zymark Inc. or equivalent. The set-up conditions and processing steps for this method using the AutoTrace Workstation are listed in Supplement B at the end of this report.

NOTE 1: In the automated method, environmental and quality-control samples are extracted in batches of six. The time required for extraction is 58 minutes. One operator typically can process 30 samples in an 8-hour day using this apparatus.

5. Reagents and consumable materials

5.1 *Helium carrier gas* (99.999 percent) as contaminant free as possible.

5.2 *Carbon dioxide gas* for drying, ultrapure.

5.3 *Nitrogen gas* for evaporation, ultrapure.

5.4 *SPE columns* packed with 500 mg of silica coated with a chemically bonded C-18 hydrocarbon phase and end-capped to reduce polar secondary interactions associated with surface silanol groups, Isolute C-18 (EC) end-capped or equivalent; International Sorbent Technology, Ltd. or equivalent. The solid packing material is held in place with stainless-steel frits.

NOTE 2: Similar columns obtained from Varian Sample Preparation Products, Bond-Elut 1212-4025, were used during initial testing of the method but were replaced by the Isolute columns because of their superior quality (see Method Performance section).

5.5 *Test tubes*, borosilicate glass, 16 mm x 100 mm, baked at 450°C for 2 hours; Kimax Brand, VWR or equivalent.

5.6 *Glass-fiber filters*, 0.7-µm nominal pore diameter (GF/F grade), baked at 450°C for 2 hours; Whatman, Inc. or equivalent.

5.7 *Glass bottles, amber*, 1,000-mL, 33-mm neck, baked at 450°C for 2 hours, fitted with Teflon-lined screw caps; NWQL GCC or equivalent.

5.8 *Solvents*: Hexane, toluene, isopropanol, methylene chloride, and methanol; B&J Brand ultrapure pesticide quality or equivalent.

5.9 *Reagent water*, ultrapure, B&J Brand for HPLC or equivalent.

5.10 Detergent solution: Prepare a dilute mixture (0.2 percent) of laboratory-grade phosphate-free liquid detergent; Liquinox, Alconox Inc. or equivalent.

6. Sampling methods, sample-collection equipment, and cleaning procedures

6.1 *Sampling methods:* Use sampling methods capable of collecting water samples that accurately represent the water-quality characteristics of the surface water or ground water at a given time or location. Detailed descriptions of sampling methods used by the U.S. Geological Survey for obtaining depth- and width-integrated surface-water samples are given in Edwards and Glysson (1988) and Ward and Harr (1990). Similar descriptions of sampling methods for obtaining ground-water samples are given in Hardy and others (1989).

6.2 *Sample-collection equipment:* Use sample-collection equipment, including automatic samplers, that are free of tubing, gaskets, and other components made of nonfluorinated plastic material that might leach interferences into water samples or sorb the pesticides and metabolites from the water. Material suitable for sample-collection equipment includes fluorinated plastics (Teflon, ETFE), metals (stainless steel, aluminum), and ceramics.

6.3 *Cleaning procedures:* Wash all sample-collection equipment with phosphate-free detergent, rinse with distilled or tap water to remove all traces of detergent, and finally rinse with ultrapure methanol (contained in a Teflon squeeze-bottle). Clean all sample-collection equipment before each sample is collected to prevent cross-contamination of the samples.

NOTE 3: Methanol needs to be collected and disposed of in accordance with local regulations.

7. Standards

7.1 *Stock standard solutions:* Obtain the pesticides, metabolites, internal standards, and surrogates as pure materials from commercial vendors. If pure materials are obtained, prepare standard solutions of about

2,000 ng/μL by accurately weighing, to the nearest 0.001 mg, 10 mg of the pure material in a 5-mL volumetric flask and dilute with ethyl acetate. Transfer the stock solutions to clean vials and store in a refrigerator. The stock solutions are stable for about 6 months.

7.2 *Primary fortification standard solution* (stock): Prepare a 40-ng/μL concentration primary fortification standard solution by combining appropriate volumes of the individual stock standard solutions in a 2- or 5-mL volumetric flask. Use adjustable micropipet (0-50 μL or 0-100 μL) to dispense an appropriate volume into the volumetric flask and dilute with toluene. Transfer the primary fortification standard solution to a clean vial and store in a refrigerator. This solution is stable for about 6 months.

7.3 *Primary dilution standard solution* (working): Prepare low-concentration (1 ng/μL) and high-concentration (10 ng/μL) primary dilution standard solutions by combining appropriate volumes of the primary fortification standard solution in a 2- or 5-mL volumetric flask and dilute with methanol. Add a 100-μL aliquot of either primary dilution standard solution to a 1-L water sample to obtain a concentration of 0.1 or 1 μg/L for the method performance-evaluation studies.

7.4 *Polyaromatic hydrocarbon (PAH) internal standard solution* (stock): Prepare a 50-ng/μL concentration of PAH internal standard solution by combining appropriate volumes of the individual stock standard solutions of acenapthalene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12} in a 2-mL volumetric flask. Use an adjustable micropipet (0-100 μL) to dispense an appropriate volume into the volumetric flask and dilute with toluene. Transfer the primary dilution standard to a clean vial and store in a refrigerator. This solution is stable for about 6 months.

7.5 *PAH internal standard solution* (working): Dilute part of the PAH internal standard stock solution to 1 ng/μL. Use an adjustable micropipet (0-100 μL) to dispense 100 μL into a 5-mL volumetric flask and dilute with toluene. Transfer the PAH internal standard solution to a clean vial and store in a refrigerator where it is stable for about 6 months.

7.6 *Surrogate solution*: Prepare a solution of Diazinon-d_{10}, *alpha*-HCH-d_6, and terbuthylazine from the stock standard solutions in methanol at a concentration of 1 ng/μL.

7.7 *Calibration solutions.* Prepare a series of calibration solutions in toluene that contain all pesticides and metabolites at concentrations from 0.01 to 40.0 ng/μL (0.01, 0.02, 0.04, 0.10, 0.20, 0.40, 1.0, 2.0, 4.0, 10, 20, 40 ng/μL) and the PAH internal standard solution at a constant concentration of 1.0 ng/μL. Prepare these calibration solutions by appropriate dilutions of the 10 and 40 ng/μL primary fortification and dilution standard solutions. For the

widely and abundantly used corn herbicides--atrazine, metolachlor, cyanazine, and alachlor--prepare a calibration solution at a concentration of 200 ng/µL and the internal standard at 1.0 ng/µL. Prepare this calibration solution by appropriate dilution of the stock standard solutions.

8. Gas chromatograph/mass spectrometer performance

8.1 Gas chromatograph performance evaluation

8.1.1 The gas chromatograph performance normally is indicated by peak shape and by the variation of the selected-compound (pesticide or metabolite) response factors relative to response factors obtained using a new capillary column and freshly prepared calibration solutions. An example of the separation and peak shape of the pesticides and metabolites is shown in a total ion chromatogram of a 1.0 ng/µL standard solution in figure 1. If peak shape deteriorates or if response factors fail to meet the calibration criteria, either change the injection liner or perform maintenance on the capillary column to bring the gas chromatograph into compliance. Part of the inlet end of the capillary column can be removed to restore performance. Specifically, a loss in response greater than 30 percent for pesticides and metabolites susceptible to loss on injection--Linuron or Carbaryl--indicates a need for immediate action.

8.2 Mass spectrometer performance evaluation

8.2.1 Check the mass spectrometer prior to analysis for the presence of water and air which indicate leaks in the vacuum. If detected, locate and fix leaks. Also, check the instrument every 24 hours during a series of analyses to ensure mass spectrometer performance according to the perfluorotributylamine (PFTBA) tuning criteria outlined below. In addition, initially adjust the mass spectrometer to ensure that the established reporting level for each selected compound can be achieved.

8.2.2 Tune the mass spectrometer daily using the procedure and standard software supplied by the manufacturer. Parameters in the tuning software are set to give ±0.15 atomic mass unit resolution at masses 69, 219, and 414 in the spectrum of PFTBA. Adjust the electron multiplier voltage to get an area of 2,000,000 counts for the mass 69 ion. Manually adjust the resolution so that the mass 69 ion has 100 percent abundance, mass 219 ion is 40±20 percent, and mass 414 ion is 6.2±5.7 percent relative abundance. Check mass assignments to ensure accuracy to ±0.15 atomic mass unit and that mass peak widths measured at one-half the peak height range from about 0.53 to 0.59 atomic mass unit.

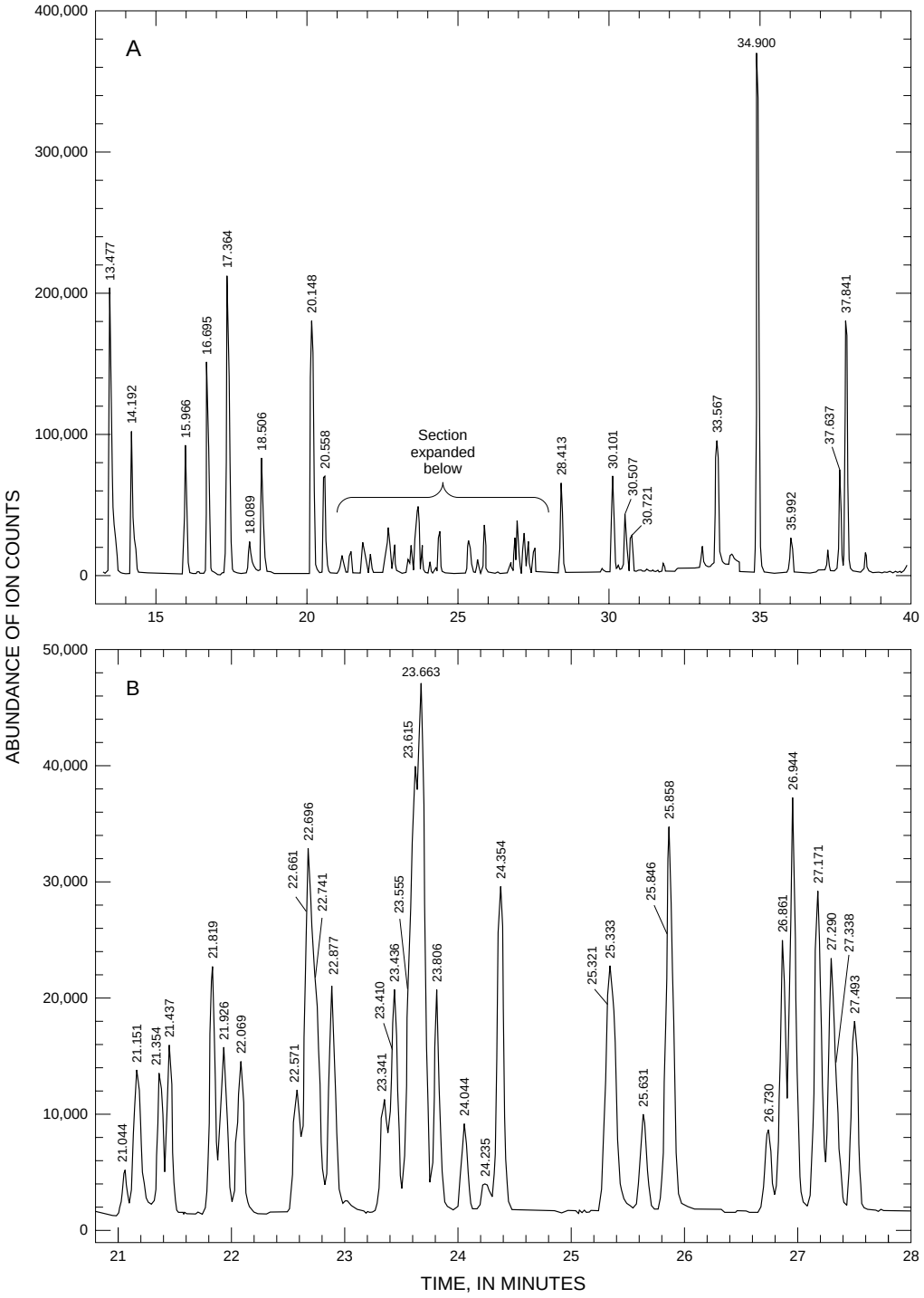

Figure 1.--A, Chromatogram of total ions of pesticides and metabolites in 1.0-nanogram-per-microliter standard solution; B, expanded view of the 21- to 28-minute time interval shown in figure 1A. Retention times shown above each peak correspond to compounds listed in table 2.

Calibration

9.1 Acquire initial calibration data by using a new capillary column and freshly prepared calibration solutions. Use these data in subsequent evaluation of the GC/MS performance.

9.2 Prior to the analysis of each sample set and every 10 samples thereafter during a series of analyses, analyze and evaluate a calibration solution (or solutions) containing all of the selected compounds to ensure that the GC/MS performance is in compliance with the established criteria.

9.3 Acquire data for each calibration solution by injecting 2 µL of each solution into the GC/MS according to the GC/MS conditions already described. Calculate the relative retention time for each selected compound and the surrogate compounds (RRT_c) in the calibration solution or in a sample as follows:

$$RRT_c = \frac{RT_c}{RT_i} \quad (1)$$

where RT_c = uncorrected retention time of the quantitation ion of the selected compound or surrogate compound, and
RT_i = uncorrected retention time of the quantitation ion of the internal standard (acenapthalene-d_{10}, phenanthrene-d_{10}, or chrysene-d_{12}, table 2).

9.4 Calculate a response factor (RF_c) for each selected compound and the surrogate compounds in each calibration solution as follows:

$$RF_c = \frac{A_c \text{ x } C_i}{C_c \text{ x } A_i} \quad (2)$$

where A_c = GC peak area of the quantitation ion for the selected compound or surrogate compounds;
C_i = concentration of the internal standard, in nanograms per microliter;
C_c = concentration of the selected compound or surrogate compounds, in nanograms per microliter; and
A_i = GC peak area of the quantitation ion for the internal standard.

9.5 See table 2 for the respective quantitation ions and internal-standard reference used in these calculations.

Table 2.--*Retention time, relative retention time, quantitation ion, and confirmation ions for selected compounds, surrogate compounds, and internal standards*

[Compounds are listed in order of retention time. min, minutes; m/z, mass per unit charge; IS, internal standard; --, not used]

Compound	Retention time (min)	Relative retention time	Quantitation ion (m/z)	Second confirmation ion (m/z)	Third confirmation ion (m/z)	Internal standard reference
Diethylanaline, 2,6-	13.477	0.766	134	149	119	IS1
EPTC	14.191	.817	128	132	189	IS1
Butylate	15.966	.919	146	156	174	IS1
Pebulate	16.695	.962	128	57	132	IS1
Tebuthiuron	18.089	1.042	156	171	88	IS1
Molinate	18.506	1.066	126	187	55	IS1
Ethalfluralin	20.044	.889	276	316	292	IS2
Ethoprop	20.558	.869	158	200	97	IS2
Propachlor	21.148	1.160	120	176	93	IS1
Atrazine, desethyl-	21.151	.894	172	174	187	IS2
Trifluralin	21.354	.902	306	264	248	IS2
Benfluralin	21.437	.906	292	318	264	IS2
Phorate	21.819	.922	75	121	231	IS2
HCH, *alpha*-	22.069	.933	181	183	219	IS2
Dimethoate	22.571	.954	125	87	93	IS2
Prometon	22.661	.958	210	183	225	IS2
Simazine	22.696	.959	201	186	173	IS2
Carbofuran	22.741	.961	164	149	127	IS2
Atrazine	22.877	.967	200	173	138	IS2
HCH, *gamma*-	23.341	.986	183	181	109	IS2
Terbufos	23.436	.990	153	186	231	IS2
Pronamide	23.555	.989	175	173	145	IS2
Fonofos	23.615	.997	109	137	246	IS2
Diazinon	23.805	1.006	137	179	153	IS2
Disulfoton	24.044	1.016	88	153	186	IS2
Terbacil	24.235	1.027	161	117	--	IS2
Triallate	24.354	1.029	86	268	145	IS2
Propanil	25.321	1.072	161	163	217	IS2
Metribuzin	25.333	1.072	198	199	144	IS2
Parathion-methyl	25.631	1.083	109	125	263	IS2
Carbaryl	25.846	1.092	144	115	116	IS2
Alachlor	25.858	1.093	160	188	237	IS2
Linuron	26.730	1.130	61	160	248	IS2
Malathion	26.861	1.135	173	127	125	IS2
Thiobencarb	26.944	1.139	100	257	125	IS2
Metolachlor	27.171	1.148	162	238	240	IS2
Cyanazine	27.278	1.153	225	240	173	IS2

Table 2.--*Retention time, relative retention time, quantitation ion, and confirmation ions for selected compounds, surrogate compounds, and internal standards*--Continued

Compound	Retention time (min)	Relative retention time	Quantitation ion (m/z)	Second confirmation ion (m/z)	Third confirmation ion (m/z)	Internal standard reference
Chlorpyrifos	27.290	1.153	197	199	314	IS2
Parathion	27.338	1.165	109	291	125	IS2
Dacthal	27.493	1.162	301	299	332	IS2
Pendimethalin	28.413	.814	252	281	162	IS3
Napropamide	30.101	.862	128	171	271	IS3
DDE, *p,p'*-	30.506	.874	246	248	318	IS3
Dieldrin	30.721	.880	79	263	265	IS3
Propargite	33.567	.962	135	173	81	IS3
Azimphos-methyl	35.992	1.034	160	132	77	IS3
Permethrin, *cis*-	37.637	1.078	183	163	165	IS3
			Surrogates			
HCH-d_6, *alpha*-	21.926	0.927	224	222	226	IS2
Terbuthylazine	23.412	.989	173	138	231	IS2
Diazinon-d_{10}	23.663	1.363	138	153	183	IS2
			Internal Standards			
Acenapthalene-d_{10} (IS1)	17.364	1	162	164	160	--
Phenanthrene-d_{10} (IS2)	23.663	1	188	--	--	--
Chrysene-d_{12} (IS3)	34.900	1	240	--	--	--

9.6 Initial calibration data acquired using a new capillary column and fresh calibration solutions are acceptable if the relative standard deviation is less than or equal to 35 percent for response factors calculated across the working concentration range for each selected compound or surrogate compounds.

NOTE 4: The concentration range suitable for the quantitation of pesticides and metabolites in this method is from 0.01 to 40 ng/µL, equivalent to 0.001 to 4.0 µg/L in a 1-L sample. Atrazine, alachlor, metolachlor, and cyanazine have an additional higher concentration standard solution, resulting in a high concentration quantitation limit of 20 µg/L.

9.7 Subsequent daily response factors calculated for the majority of compounds need to agree within ±20 percent of the average response factor for the selected compound of interest. Analyze at least one calibration solution with each sample set, and analyze a standard near or at the detection limit at least once weekly to verify that the detection limits are being achieved.

9.8 Add the latest response factors to prior response factors and calculate a new average response factor, provided the latest data meet the criteria given above, and the relative standard deviation for all of the response-factor data is less than or equal to 35 percent.

9.9 Calibration-curve fitting routines also can be used, provided back calculation of the calibration-standard concentration agrees within ±20 percent of the expected value.

10. Procedure

10.1 *Weighing SPE columns* (optional): Weigh the SPE columns (±0.0001 g) and record the weight on the column using waterproof ink.

NOTE 5: Recording the weight on the SPE columns helps to determine when the columns are dry after extraction and drying steps.

10.2 *Precleaning SPE columns*: Preclean the SPE columns by rinsing with 3 mL of the elution solvent (hexane-isopropanol 3:1). Allow the solvent to drain by gravity, then completely remove all solvent from the column by either nitrogen positive pressure or vacuum. Use a vacuum/elution apparatus to remove solvent by vacuum. Attach the SPE columns to the Luer-Lok fittings and twist counterclockwise to open the fittings. An optional Benchmate Workstation also can be used for automated cleaning of the columns in batches of 50. Store the clean columns in 40-mL glass vials until used.

10.3 *Precleaning extraction apparatus*: Set up the solid-phase-extraction pumping apparatus as shown in figure 2. Use a 50-mL glass graduated cylinder to contain the cleaning solutions and prevent contamination of the inlet tubing. Rinse the Teflon-PFA tubing and pump with about 50 mL of detergent solution, followed by about 100 mL of tap water and 50 mL of methanol. Turn on the pump and adjust the flow rate of the pump to 20 to 25 mL/min using a graduated cylinder to measure the volume through the SPE column. Ensure there are no leaks in any of the fittings. Keep the clean inlet tubing of the pump in the glass cylinder to avoid contamination of the tubing while preparing the sample and SPE column. For longer storage, wrap the tubing in aluminum foil.

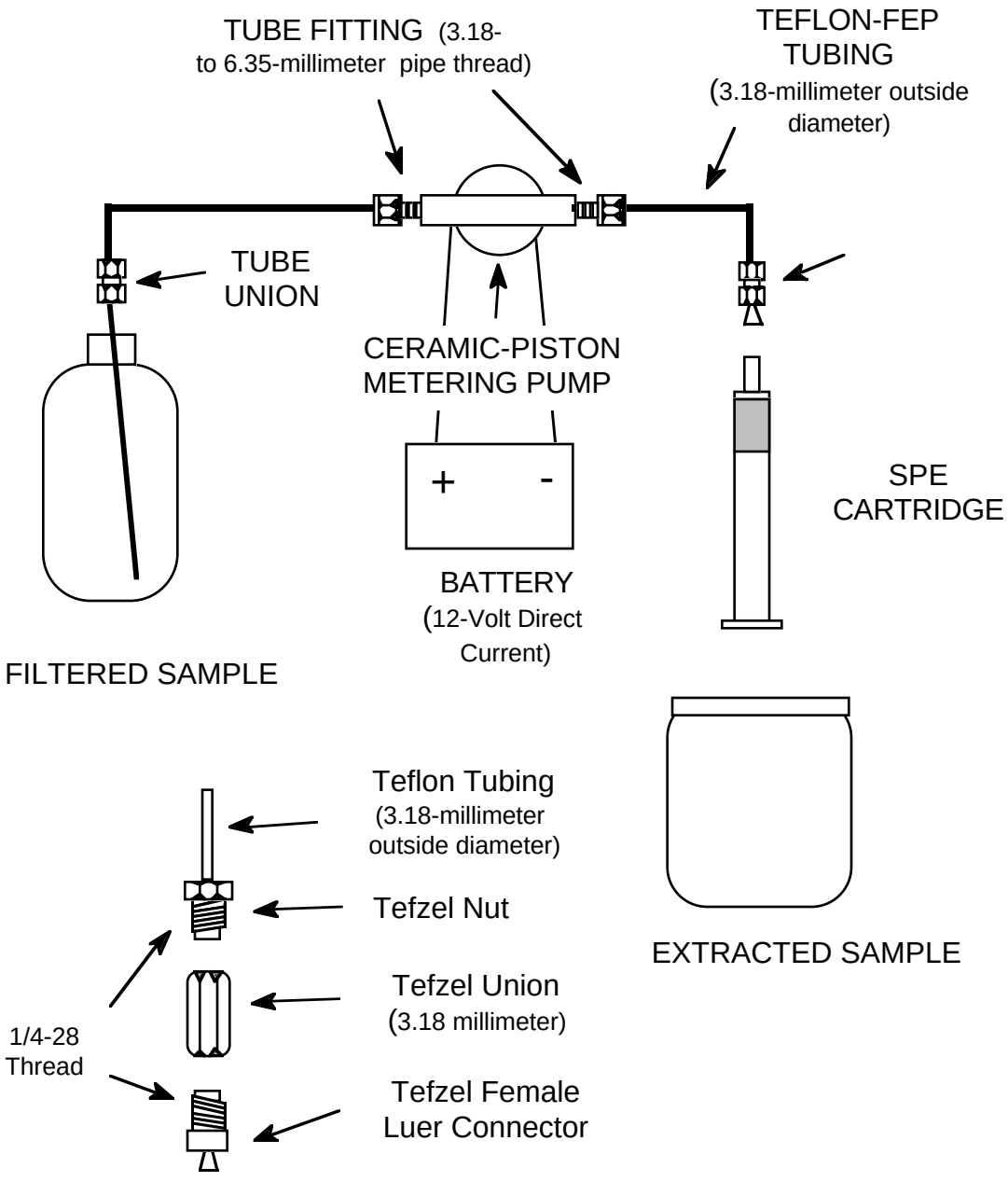

Figure 2.--Manual solid-phase-extraction pumping apparatus.

10.4 *SPE column conditioning*: Immediately before sample extraction, add 3 mL of methanol to the SPE column and allow the methanol to partially drain through the column by gravity. An optional Luer flow-control valve attached to the male Luer fitting of the SPE column can be used to control the flow of fluids through the SPE column. Conditioning is needed to solvate the C-18 phase attached to the silica particles in the SPE column. This conditioning ensures maximum interaction of the C-18 phase with the sample.

NOTE 6: Do not allow the columns to go dry once conditioning has started. Maintain levels of fluids by adding additional fluid or by closing Luer-Lok fittings or flow-control values.

10.5 *SPE column equilibration*: Replace the methanol in the SPE column with ultrapure water to equilibrate the column with the sample matrix. Add 3 mL of ultrapure water and allow the water and methanol to partially drain through the column by gravity. About 5 minutes is required for each volume of the water and methanol to drip through the column.

10.6 *Sample preparation*: Water samples must have been previously filtered (Sandstrom, 1995). Weigh the sample and bottle and record the gross sample weight (±1 g). To the sample, add methanol equivalent to 1 percent of the sample volume (about 9 mL) as a conditioner, and record the gross sample weight. Add a 100-µL aliquot of the surrogate solution (1 ng/µL) using a micropipet with a disposable glass bore. (This should result in a concentration of 0.1 µg/L for the surrogates in a 1-L sample.) Swirl the sample in the bottle to thoroughly mix.

NOTE 7: Allow surrogate and spike solutions to come to room temperature before adding to samples.

10.7 *Sample extraction*: Weigh a 1,000-mL plastic beaker that will be used to collect the volume of sample processed through the column. Place the inlet end of the Teflon-PFA tubing into the sample container, making sure tubing end is positioned in lowest spot of the bottle, and turn on the pump. After all air is displaced from the tubing, attach the SPE column to the outlet fitting of the pump tubing, and collect the sample that is pumped through the column. Ensure that there are no leaks or sources of bubbles in the system. Small bubbles might form as the sample is pumped through the tubing, but they will not cause any problems if they accumulate in the pump head. Large air bubbles are a problem because they can displace the methanol conditioner in the column or cause uneven flow through the column.

NOTE 8: To avoid contaminating the sample, do not handle the outside of the clean section of tubing that is placed in the sample bottle. A piece of tape attached to the top of the tubing helps to indicate which section of the tubing can be handled and which is clean and will be in contact with the sample.

10.8 Pump all of the sample through the SPE column and turn off the pump when completed. Disconnect the column from the pump system and remove residual interstitial water with a positive pressure of air. Weigh the extracted water sample, and record the final weight of the sample processed through the column. Discard the extracted sample, weigh the empty sample bottle, and record the tare weight.

10.9 Clean the pump and Teflon-PFA tubing with detergent solution, water, and methanol (see section 6.3) to prepare for the next sample.

10.10 *SPE column drying*: Attach a universal adapter to the large, open end of the SPE column. Next attach the adapter to the male Luer-Lok fitting on the gas-pressure module of the SPE vacuum manifold, and then dry the column using a positive pressure (138 kPa or 20 lb/in^2 for 20 minutes) of ultrapure carbon dioxide to remove all interstitial water. Ultrapure nitrogen gas also can be used to dry the column, but the drying time might be longer. Optional: Verify that all water is removed from the column by periodically weighing the column and comparing the weight to the pre-extraction weight.

NOTE 9: Do not dry the column for excessive periods of time. Pesticides and metabolites might evaporate and be removed in the gas phase.

10.11 *Elution of compounds*: Label a 16- x 100-mm culture tube with sample identification and place in a holding rack. Add 100 µL of the internal standard PAH solution (1 ng/µL) to the culture tube using a micropipet or syringe. Place the dried SPE columns in the appropriate culture tube. The open end of the SPE column rests on the edge of the culture tube, keeping the male Luer end of the SPE column raised a few centimeters above the bottom of the culture tube. Add 3 mL of HIP (3:1) to the SPE column and allow the solvent to drain by gravity into the culture tube (about 5 minutes). Air pressure (using a 50-mL glass syringe) can be used to gently force interstitial solvent remaining in the column into the vial.

10.12 *Evaporation of solvent:* Preheat the TurboVap evaporator water bath to 30°C, and adjust the gas pressure to 34.5 kPa (5 lb/in^2). Place culture tubes in the TurboVap evaporator for about 15 minutes and concentrate the eluant to about 100 µL under a gentle stream of nitrogen. Periodically check the sample volumes. At no time should the eluant be allowed to evaporate completely, because this might result in loss of compounds.

10.13 *Transfer to vials*: Using a baked disposable glass Pasteur pipet, withdraw eluant into pipet, and transfer eluant to appropriately labeled GC vial containing a 200-µL insert for GC/MS analysis.

NOTE 10: A glass syringe fitted with a short length of silicone tubing to attach the glass Pasteur pipet is the preferred procedure for withdrawing eluant into the pipet. Solvent vapors in contact with rubber or latex pipet bulbs might contaminate the eluant with plasticizers.

10.14 Rinse the culture tube with 50 µL of toluene, using a syringe to dispense the solvent, and taking care not to allow the tip of the syringe to contact the walls of the culture tube. If the tip does contact the culture tube, rinse with solvent. Vortex the culture tube, ensuring the solvent reaches the height of the original 3-mL solvent volume. Transfer the toluene rinse into the GC vial insert. Cap GC vial, and refrigerate until analysis by GC/MS.

NOTE 11: Using a pipet or squeeze bottle to rinse the culture tube is not good practice because this might result in excess solvent added and require additional evaporation.

10.15 *Sample analysis and data evaluation*: Ensure that GC/MS conditions for the analysis of the selected compounds in sample extracts are the same as those used in the analysis of the calibration solutions. Prior to the analysis of any sample extracts, ensure that the PFTBA mass-spectral performance criteria have been met, and that the selected-compound calibration data conform to the criteria set forth above. In addition, optimize the system so the reporting level for each selected compound can be achieved. Inject 2 µL of the sample extract and acquire data using the GC/MS conditions described in sections 4.14.1 and 4.14.2.

11. Calculation of results

11.1 Qualitative identification

11.1.1 The expected retention time (RT) of the GC peak of the quantitation ion for the selected compound of interest needs to be within ±6 seconds of the expected retention time based on the RRT_c obtained from the internal-standard analysis. Calculate the expected retention time as follows:

$$RT = RRT_c \times RT_i \qquad (3)$$

where RT = expected retention time of the selected compound or surrogate compound,
RRT_c = relative retention time of the selected compound or surrogate compound, and
RT_i = uncorrected retention time of the quantitation ion of the internal standard.

11.1.2 Mass-spectral verification for each selected compound is done by comparing the relative integrated abundance values of the three significant ions monitored with the relative integrated abundance values obtained from calibration solutions analyzed by the GC/MS according to procedures given above. The relative ratios of the three ions need to be within ±20 percent of the relative ratios of those obtained on injection of a 1-ng calibration solution in the absence of any obvious interferences.

11.2 Quantitation

11.2.1 Calculate the weight of sample processed as follows:

$$W = (W_a - W_c) \times \frac{W_s - W_b}{W_m - W_b} \quad (4)$$

where W = weight of sample, in grams;
W_a = weight of sample and container after SPE, in grams;
W_c = weight of container used to collect sample that passes through SPE column, in grams;
W_s = weight of bottle and sample, in grams;
W_b = weight of empty sample bottle, in grams; and
W_m = weight of sample, methanol, and bottle, in grams.

11.2.2 If a selected compound has passed the aforementioned qualitative identification criteria, calculate the concentration in the sample as follows:

$$C = \frac{C_i \times A_c \times 1000}{F_c \times A_i \times W} \quad (5)$$

where C = concentration of the selected compound or surrogate compound in the sample, in micrograms per liter;
C_i = mass of the corresponding internal standard, in micrograms per sample;
A_c = area of the quantitation ion for the selected compound or surrogate compound identified;
F_c = response factor for each selected compound or surrogate compound calculated above;
A_i = area of the quantitation ion for the internal standard; and
W = volume of the sample, in milliliters (assume 1.0 g = 1.0 mL).

11.2.3 The percent recovery of the surrogate compounds is calculated as follows:

$$R = \frac{C_i \text{ x } A_c}{RF_c \text{ x } A_i \text{ x } C_s \text{ x } V_s} \text{ x } 100 \quad (6)$$

where R = percent recovery of the surrogate compound;
C_i = mass of the corresponding internal standard, in nanograms per sample;
A_c = area of the quantitation ion for the surrogate compound;
RF_c = response factor for the surrogate compound;
A_i = area of the quantitation ion for the internal standard;
C_s = concentration of the surrogate compound in the surrogate standard solution added to the sample, in nanograms per microliter; and
V_s = volume of the surrogate standard solution added to the sample, in microliters.

11.3 Reporting of results

This method was designed for use in studies of pesticide occurrence and transport, for which the best possible information about the presence and concentration of a pesticide is needed even if the standard error is relatively high. Consequently, results are not censored at a low reporting level. Concentrations of pesticides are reported as follows: If the concentration is less than the MDL listed in table 9, report the concentration to three significant figures, using the "E" code to alert the user that the result is less than the statistically determined MDL; if the concentration is greater than the detection limit, report the concentration to three significant figures; if the concentration is greater than the highest concentration standard, report the result as "greater than the highest standard," for example, >4 µg/L.

METHOD PERFORMANCE

A reagent-water sample, a surface-water sample collected from the South Platte River near Henderson, Colo., and a ground-water sample collected in Jefferson County, Colo. (monitoring well near building 15, Denver Federal Center) were used to test the method performance. Each of the three samples was split into 14 1-L subsamples. One set of seven subsamples was fortified with 0.1 µg/L of each compound and the other set of seven subsamples was fortified with 1.0 µg/L of each compound. In addition, unfortified samples of the surface water and ground water were extracted and analyzed to determine background concentrations of the pesticides. All subsamples were analyzed in one laboratory (the National Water Quality Laboratory) using one GC/MS.

Each sample set was extracted and analyzed on different days during September 1992, so comparison of different matrices and concentrations includes bias from day-to-day variation. Accuracy and precision data from the analyses are listed in tables 3 through 8.

Rejection of outlier samples: If the concentration of more than one replicate determination from a subsample was consistently high or low, it was assumed there was a systematic error with that sample, and the data were not included in calculating the method performance. One replicate was rejected in both the 0.1-µg/L concentration in the reagent-water data set and in the 1.0-µg/L concentration in the ground-water data set, so only six replicates were used to evaluate method performance.

Rejection of individual compound outliers: If the relative standard deviation for any concentration-matrix specific data set was greater than 10 percent, extreme values were tested as outliers using a standard Student's *t*-test (American Society for Testing and Materials, 1993). Outliers were rejected if the *t*-value exceeded the critical *t*-value [t = 2.14, 7 degrees of freedom, α=0.01 (99-percent confidence level)]. Using this approach, two results were rejected as outliers (tables 4 and 9).

Corrections for background concentrations: The ground-water sample did not require correction for background concentrations of compounds. The surface-water sample contained low concentrations of atrazine (0.043 µg/L), simazine (0.022 µg/L), Terbufos (0.059 µg/L), pronamide (0.074 µg/L), Diazinon (0.062 µg/L), Carbaryl (0.18 µg/L), and tebuthiuron (0.12 µg/L). These concentrations are subtracted from values determined to give corrected results in tables 5 and 6.

Method detection limits: The MDL is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99-percent confidence that the compound concentration is greater than zero (Wershaw and others, 1987). MDLs were determined according to procedures outlined by the U.S. Environmental Protection Agency (1992). Seven replicate samples of reagent water fortified at 0.1 µg/L were analyzed to determine a preliminary estimated MDL (table 3).

The MDL was calculated using the following equation:

$$MDL = S \times t_{(n-1,\ 1-\alpha = 0.99)}$$

where S = standard deviation of replicate analyses, in micrograms per liter, at the lowest concentration;

n = number of replicate analyses; and

$t_{(n-1,\ 1-\alpha = 0.99)}$ = Student's *t*-value for the 99-percent confidence level with $n-1$ degrees of freedom (U.S. Environmental Protection Agency, 1992).

Table 3.--*Recovery and precision data from six determinations of the compounds at 0.1 microgram per liter in reagent water*

[conc., concentration; µg/L, microgram per liter; MDL, method detection limit; E code, estimated value; --, MDL not determined for surrogates]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)	Preliminary estimated MDL (µg/L)
Alachlor	0.086	0.003	3	86	0.009
Atrazine	.089	.005	6	89	.017
Benfluralin	.046	.004	9	46	.013
Butylate	.080	.002	3	80	.008
Chlorpyrifos	.083	.002	2	83	.005
Cyanazine	.096	.004	4	96	.013
Dacthal	.082	.001	2	82	.004
DDE, *p,p'*-	.048	.003	6	48	.010
Diazinon	.077	.002	3	77	.008
Dieldrin	.067	.003	4	67	.008
Diethylanaline, 2,6-	.073	.002	3	73	.006
Disulfoton	.072	.003	4	72	.008
EPTC	.080	.002	2	80	.005
Ethalfluralin	.054	.004	8	54	.013
Ethoprop	.080	.004	5	80	.012
Fonofos	.075	.002	3	75	.008
HCH, *alpha*-	.077	.002	3	77	.007
HCH, *gamma*-	.077	.003	4	77	.011
Linuron	.126	.012	10	126	.039
Malathion	.090	.005	5	90	.014
Metolachlor	.092	.003	3	92	.009
Metribuzin	.042	.004	9	42	.012
Molinate	.082	.002	3	82	.007
Napropamide	.083	.003	4	83	.010
Parathion	.083	.007	9	83	.022
Parathion-methyl	.073	.011	15	73	.035
Pebulate	.079	.003	4	79	.009
Pendimethalin	.046	.006	13	46	.018
Permethrin, *cis*-	.037	.005	13	37	.016
Phorate	.077	.003	4	77	.011
Prometon	.077	.003	3	77	.008
Pronamide	.076	.003	4	76	.009
Propachlor	.079	.005	6	79	.015
Propanil	.096	.005	5	96	.016
Propargite	.059	.002	3	59	.006
Simazine	.076	.003	3	76	.008
Tebuthiuron	.088	.005	6	88	.015
Terbufos	.074	.004	5	74	.012
Thiobencarb	.085	.003	3	85	.008
Triallate	.075	.003	4	75	.008
Trifluralin	.047	.004	8	47	.012

Table 3.--*Recovery and precision data from six determinations of the compounds at 0.1 microgram per liter in reagent water*--Continued

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)	Preliminary estimated MDL (µg/L)
Pesticides having poor performance and reported with an E code					
Atrazine, desethyl-	0.012	0.001	8	12	0.003
Azimphos-methyl	.078	.012	15	78	.038
Carbaryl	.151	.014	10	151	.046
Carbofuran	.108	.004	4	108	.013
Terbacil	.075	.010	13	75	.030
Pesticide deleted from method in November 1994					
Dimethoate	0.011	0.008	68	11	0.024
Surrogates					
HCH-d_6, *alpha*-	0.905	0.015	2	90	--
Diazinon-d_{10}	.876	.024	3	88	--
Terbuthylazine	1.000	.022	2	100	--

Table 4.--*Recovery and precision data from seven determinations of the compounds at 1.0 microgram per liter in reagent water*

[conc., concentration; µg/L, microgram per liter; E code, estimated value]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Alachlor	0.861	0.039	5	86
Atrazine	.840	.046	5	84
Benfluralin	.483	.033	7	48
Butylate	.769	.035	5	77
Carbaryl	2.020	.204	10	202
Carbofuran	1.261	.066	5	126
Chlorpyrifos	.784	.053	7	78
Cyanazine	.901	.047	5	90
Dacthal	.829	.046	6	83
DDE, *p,p'*-	.371	.049	13	37
Diazinon	.779	.041	5	78
Dieldrin	.600	.030	5	60
Diethylanaline, 2,6-	.694	.038	6	69
Disulfoton	.757	.034	5	76
EPTC	.780	.035	5	78
Ethalfluralin	.532	.035	7	53

Table 4.--*Recovery and precision data from seven determinations of the compounds at 1.0 microgram per liter in reagent water*--Continued

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Ethoprop	0.793	0.027	3	79
Fonofos	.777	.033	4	78
HCH, *alpha*-	.739	.030	4	74
HCH, *gamma*-	.766	.032	4	77
Linuron[1]	1.173	.032	3	117
Malathion	.961	.047	5	96
Metolachlor	.891	.044	5	89
Metribuzin	.345	.018	5	35
Molinate	.753	.027	4	75
Napropamide	.718	.027	4	72
Parathion	.905	.056	6	90
Parathion-methyl	.924	.052	6	92
Pebulate	.762	.032	4	76
Pendimethalin	.521	.036	7	52
Permethrin, *cis*-	.343	.064	19	34
Phorate	.737	.028	4	74
Prometon	.671	.046	7	67
Pronamide	.842	.042	5	84
Propachlor	.786	.028	4	79
Propanil	.908	.048	5	91
Propargite	.506	.050	10	51
Simazine	.612	.033	5	61
Tebuthiuron[1]	.936	.052	6	94
Terbufos	.714	.033	5	71
Thiobencarb	.841	.047	6	84
Triallate	.733	.038	5	73
Trifluralin	.489	.033	7	49
Pesticides having poor performance and reported with an E code				
Atrazine, desethyl-	0.091	0.006	6	9
Azimphos-methyl	.889	.051	6	89
Carbaryl	2.020	.204	10	202
Carbofuran	1.261	.066	5	126
Terbacil	.577	.032	6	58
Pesticide deleted from method in November 1994				
Dimethoate	0.052	0.005	10	5
Surrogates				
HCH-d_6, *alpha*-	0.954	0.042	4	95
Diazinon-d_{10}	1.002	.058	6	100
Terbuthylazine	1.075	.060	6	107

[1]Six replicates were used for accuracy and precision data after rejection of one concentration (linuron, 1.400 µg/L; tebuthiuron, 0.465 µg/L) as an outlier based on Student's *t*-test (American Society for Testing and Materials, 1993).

Table 5.--*Recovery and precision data from seven determinations of the compounds at 0.1 microgram per liter in surface water (South Platte River near Henderson, Colo.)*

[conc., concentration; µg/L, microgram per liter; --, no data; E code, estimated value]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Alachlor	0.095	0.006	6	95
Atrazine[1]	.060	.007	12	60
Benfluralin	.060	.006	9	60
Butylate	.085	.010	11	85
Chlorpyrifos	.080	.008	10	80
Cyanazine	.066	.003	5	66
Dacthal	.087	.007	8	87
DDE, *p,p'*-	.045	.007	15	45
Diazinon[1]	.068	.009	13	68
Dieldrin	.062	.005	9	62
Diethylanaline, 2,6-	.067	.006	9	67
Disulfoton	.141	.005	3	141
EPTC	.083	.004	5	83
Ethalfluralin	.068	.006	9	68
Ethoprop	.096	.011	12	96
Fonofos	.073	.005	7	73
HCH, *alpha*-	.077	.005	7	77
HCH, *gamma*-	.072	.005	7	72
Linuron	.037	.002	5	37
Malathion	.085	.006	7	85
Metolachlor	.087	.004	5	87
Metribuzin	.056	.004	7	56
Molinate	.081	.004	5	81
Napropamide	.079	.004	5	79
Parathion	.068	.006	8	68
Parathion-methyl	.071	.006	8	71
Pebulate	.081	.004	5	81
Pendimethalin	.064	.004	7	64
Permethrin, *cis*-	.039	.006	16	39
Phorate	.105	.005	5	105
Prometon	.098	.011	11	98
Pronamide[1]	.046	.010	22	46
Propachlor	.082	.006	7	82
Propanil	.083	.008	10	83
Propargite	.056	.005	9	56
Simazine[1]	.058	.005	8	58
Tebuthiuron[1]	--	--	--	--
Terbufos	.046	.004	9	46
Thiobencarb	.076	.006	8	76
Triallate	.071	.005	7	71
Trifluralin	.063	.004	7	63

Table 5.--*Recovery and precision data from seven determinations of the compounds at 0.1 microgram per liter in surface water (South Platte River near Henderson, Colo.)*--Continued

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Pesticides having poor performance and reported with an E code				
Atrazine, desethyl-	0.019	0.002	9	19
Azimphos-methyl	.042	.006	14	42
Carbaryl	.010	.032	335	10
Carbofuran	.119	.006	5	119
Terbacil	.125	.010	8	125
Pesticide deleted from method in November 1994				
Dimethoate	0.034	0.006	17	34
Surrogates				
HCH-d_6, *alpha*-	0.844	0.044	5	84
Diazinon-d_{10}	.851	.057	7	85
Terbuthylazine	.789	.042	5	79

[1]Corrected for background concentrations of compound in surface water.

Table 6.--*Recovery and precision data from seven determinations of the compounds at 1.0 microgram per liter in surface water (South Platte River near Henderson, Colo.)*

[conc., concentration; µg/L, microgram per liter; E code, estimated value]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Alachlor	0.827	0.036	4	83
Atrazine[1]	.769	.028	4	77
Benfluralin	.619	.058	9	62
Butylate	.853	.023	3	85
Chlorpyrifos	.671	.040	6	67
Cyanazine	.629	.034	5	63
Dacthal	.821	.035	4	82
DDE, *p,p'*-	.397	.051	13	40
Diazinon[1]	.763	.027	4	76
Dieldrin	.577	.045	8	58
Diethylanaline, 2,6-	.738	.018	2	74
Disulfoton	.746	.020	3	75
EPTC	.861	.022	3	86
Ethalfluralin	.645	.046	7	65

Table 6.--*Recovery and precision data from seven determinations of the compounds at 1.0 microgram per liter in surface water (South Platte River near Henderson, Colo.)*--Continued

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Ethoprop	0.835	0.028	3	84
Fonofos	.738	.019	3	74
HCH, *alpha*-	.654	.016	2	65
HCH, *gamma*-	.756	.022	3	76
Linuron	.257	.023	9	26
Malathion	.761	.037	5	76
Metolachlor	.880	.033	4	88
Metribuzin	.430	.017	4	43
Molinate	.845	.024	3	85
Napropamide	.803	.010	1	80
Parathion	.680	.032	5	68
Parathion-methyl	.619	.030	5	62
Pebulate	.864	.023	3	86
Pendimethalin	.647	.054	8	65
Permethrin, *cis*-	.316	.047	15	32
Phorate	.742	.018	2	74
Prometon	.670	.061	9	67
Pronamide[1]	1.147	.040	3	115
Propachlor	.816	.035	4	82
Propanil	.770	.031	4	77
Propargite	.566	.067	12	57
Simazine[1]	.657	.028	4	66
Tebuthiuron[1]	.653	.060	9	65
Terbufos	.696	.025	4	70
Thiobencarb	.761	.029	4	76
Triallate	.703	.022	3	70
Trifluralin	.635	.057	9	64
Pesticides having poor performance and reported with an E code				
Atrazine, desethyl-	0.100	0.006	6	10
Azimphos-methyl	.233	.024	10	23
Carbaryl	.747	.039	5	75
Carbofuran	.925	.031	3	93
Terbacil	.833	.027	3	83
Pesticide deleted from method in November 1994				
Dimethoate	0.066	0.009	14	7
Surrogates				
HCH-d_6, *alpha*-	0.771	0.025	3	77
Diazinon-d_{10}	.809	.053	6	81
Terbuthylazine	.739	.039	5	74

[1]Corrected for background concentrations of compound in surface water.

Table 7.--*Reocvery and precision data from seven determinations of the compounds at 0.1 microgram per liter in ground water (Denver Federal Center Well 15)*

[conc., concentration; µg/L, microgram per liter; E code, estimated value]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Alachlor	0.089	0.003	3	89
Atrazine	.079	.002	3	79
Benfluralin	.045	.005	10	45
Butylate	.077	.003	3	77
Chlorpyrifos	.074	.005	6	74
Cyanazine	.079	.003	4	79
Dacthal	.079	.003	4	79
DDE, *p,p'*-	.051	.012	23	51
Diazinon	.070	.002	3	70
Dieldrin	.063	.008	13	63
Diethylanaline, 2,6-	.065	.003	4	65
Disulfoton	.132	.003	2	132
EPTC	.077	.001	2	77
Ethalfluralin	.043	.003	7	43
Ethoprop	.073	.003	4	73
Fonofos	.065	.002	3	65
HCH, *alpha*-	.070	.002	2	70
HCH, *gamma*-	.076	.003	4	76
Linuron	.042	.006	14	42
Malathion	.072	.004	5	72
Metolachlor	.082	.004	4	82
Metribuzin	.041	.003	6	41
Molinate	.082	.003	4	82
Napropamide	.080	.005	6	80
Parathion	.054	.004	7	54
Parathion-methyl	.047	.002	5	47
Pebulate	.079	.003	3	79
Pendimethalin	.046	.005	11	46
Permethrin, *cis*-	.040	.009	23	40
Phorate	.089	.003	4	89
Prometon	.050	.002	4	50
Pronamide	.098	.004	4	98
Propachlor	.083	.004	4	83
Propanil	.073	.003	4	73
Propargite	.055	.006	11	55
Simazine	.073	.003	4	73
Tebuthiuron	.071	.002	3	71
Terbufos	.094	.005	5	94
Thiobencarb	.074	.003	4	74
Triallate	.067	.003	4	67
Trifluralin	.044	.004	9	44

Table 7.--*Recovery and precision data from seven determinations of the compounds at 0.1 microgram per liter in ground water (Denver Federal Center Well 15)*--Continued

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Pesticides having poor performance and reported with an E code				
Atrazine, desethyl-	0.014	0.001	6	14
Azimphos-methyl	.054	.005	9	54
Carbaryl	.094	.007	8	94
Carbofuran	.100	.005	5	100
Terbacil	.110	.005	5	110
Pesticide deleted from method in November 1994				
Dimethoate	0.025	0.005	21	25
Surrogates				
HCH-d_6, *alpha*-	0.824	0.030	4	82
Diazinon-d_{10}	.998	.035	4	100
Terbuthylazine	.853	.025	3	85

Table 8.--*Recovery and precision data from six determinations of the compounds at 1.0 microgram per liter in ground water (Denver Federal Center Well 15)*

[conc., concentration; µg/L, microgram per liter; E code, estimated value]

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Alachlor	0.893	0.034	4	89
Atrazine	.766	.027	4	77
Benfluralin	.568	.050	9	57
Butylate	.699	.011	2	70
Chlorpyrifos	.690	.054	8	69
Cyanazine	.733	.045	6	73
Dacthal	.809	.045	6	81
DDE, *p,p'*-	.506	.035	7	51
Diazinon	.742	.069	9	74
Dieldrin	.624	.051	8	62
Diethylanaline, 2,6-	.639	.017	3	64
Disulfoton	.739	.037	5	74
EPTC	.697	.016	2	70
Ethalfluralin	.528	.038	7	53

Table 8.--*Recovery and precision data from six determinations of the compounds at 1.0 microgram per liter in ground water (Denver Federal Center Well 15)*--Continued

Compound	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)
Ethoprop	0.750	0.036	5	75
Fonofos	.701	.032	5	70
HCH, *alpha*-	.586	.021	4	59
HCH, *gamma*-	.740	.041	6	74
Linuron	.330	.164	50	33
Malathion	.707	.027	4	71
Metolachlor	.786	.030	4	79
Metribuzin	.429	.020	5	43
Molinate	.736	.007	1	74
Napropamide	.732	.081	11	73
Parathion	.572	.020	4	57
Parathion-methyl	.530	.017	3	53
Pebulate	.712	.011	2	71
Pendimethalin	.550	.036	6	55
Permethrin, *cis*-	.418	.043	10	42
Phorate	.584	.016	3	58
Prometon	.459	.022	5	46
Pronamide	.996	.036	4	100
Propachlor	.762	.007	1	76
Propanil	.714	.033	5	71
Propargite	.900	.124	14	90
Simazine	.683	.023	3	68
Tebuthiuron	.532	.052	10	53
Terbufos	.605	.015	2	60
Thiobencarb	.710	.035	5	71
Triallate	.713	.039	5	71
Trifluralin	.541	.034	6	54
Pesticides having poor performance and reported with an E code				
Atrazine, desethyl-	0.122	0.007	5	12
Azimphos-methyl	.519	.041	8	52
Carbaryl	.864	.073	8	86
Carbofuran	.881	.046	5	88
Terbacil	.763	.022	3	76
Pesticide deleted from method in November 1994				
Dimethoate	0.098	0.011	12	10
Surrogates				
HCH-d_6, *alpha*-	0.885	0.050	6	89
Diazinon-d_{10}	.934	.034	4	93
Terbuthylazine	.874	.045	5	87

Table 9.--*Method detection limit calculated from precision data for seven determinations of the compounds in reagent water fortified at initial detection limits estimated in table 3*

[MDL, method detection limit; conc., concentration, µg/L, microgram per liter; E code, estimated value]

Compound	MDL expected conc. (µg/L)	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)	Method detection limit (µg/L)
Alachlor	0.01	0.011	0.0005	4	113	0.002
Atrazine[1]	.01	.010	.0004	4	98	.001
Benfluralin	.02	.010	.0005	5	51	.002
Butylate	.01	.008	.0005	6	84	.002
Chlorpyrifos	.01	.012	.0013	11	116	.004
Cyanazine	.02	.014	.0013	9	71	.004
Dacthal	.01	.016	.0005	3	156	.002
DDE, *p,p'*-	.03	.034	.0019	6	113	.006
Diazinon	.02	.017	.0007	4	84	.002
Dieldrin	.03	.027	.0004	1	90	.001
Diethylanaline, 2,6-	.01	.005	.0010	20	47	.003
Disulfoton	.30	.247	.0053	2	82	.017
EPTC	.01	.008	.0005	6	84	.002
Ethalfluralin	.02	.020	.0013	6	102	.004
Ethoprop	.02	.017	.0010	6	84	.003
Fonofos	.02	.016	.0008	5	80	.003
HCH, *alpha*-	.03	.029	.0005	2	95	.002
HCH, *gamma*-	.03	.030	.0012	4	100	.004
Linuron	.05	.011	.0007	6	22	.002
Malathion	.03	.021	.0017	8	71	.005
Metolachlor	.01	.011	.0006	5	110	.002
Metribuzin	.04	.023	.0012	5	57	.004
Molinate	.02	.018	.0012	6	90	.004
Napropamide	.02	.025	.0010	4	124	.003
Parathion	.03	.017	.0014	8	58	.004
Parathion-methyl	.03	.014	.0018	13	46	.006
Pebulate	.03	.023	.0013	5	78	.004
Pendimethalin	.04	.017	.0014	8	42	.004
Permethrin, *cis*-	.05	.025	.0016	6	50	.005
Phorate	.02	.015	.0008	5	76	.002
Prometon	.04	.018	.0058	32	45	.018
Pronamide	.03	.021	.0010	4	71	.003
Propachlor	.01	.010	.0021	21	100	.007
Propanil	.02	.015	.0011	8	73	.004
Propargite	.04	.026	.0040	16	64	.013
Simazine	.03	.028	.0017	6	94	.005
Tebuthiuron	.03	.032	.0030	10	106	.010
Terbufos	.03	.042	.0040	10	139	.013
Thiobencarb	.03	.027	.0008	3	91	.002
Triallate	.01	.009	.0004	4	91	.001
Trifluralin	.02	.012	.0008	6	59	.002

Table 9.--*Method detection limit calculated from precision data for seven determinations of the compounds in reagent water fortified at initial detection limits estimated in table 3*--Continued

Compound	MDL expected conc. (µg/L)	Mean observed conc. (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Mean recovery (percent)	Method detection limit (µg/L)
Pesticides having poor performance and reported with an E code						
Atrazine, desethyl-	0.05	0.008	0.0007	8	16	0.002
Azimphos-methyl	.03	.004	.0000	0	13	.001
Carbaryl	.03	.007	.0011	15	24	.003
Carbofuran	.02	.006	.0011	18	31	.003
Terbacil	.03	.012	.0022	19	39	.007
Pesticide deleted from method in November 1994						
Dimethoate	0.07	0.013	0.0014	11	19	0.004

[1]Six determinations were used for mean concentration and standard deviation after rejection of one concentration (0.016 µg/L) as an outlier based on a Student's *t*-test (American Society for Testing and Materials, 1993).

The preliminary estimated MDLs ranged from 0.004 to 0.039 µg/L (table 3). According to the U.S. Environmental Protection Agency (1992) procedure, the fortified concentrations should be no more than five times the estimated MDL. Because the fortified concentration (0.1 µg/L) was more than five times the estimated MDLs for many of the pesticides in table 3, another MDL determination was conducted by fortifying seven replicates with the compounds at the estimated MDLs determined in table 3. The MDLs calculated from this procedure range from 0.001 to 0.018 µg/L (table 9). The MDLs in table 9 are used as the default reporting value when no peak is observed at the characteristic retention time.

The MDLs do not account for sample matrix. With clean environmental samples, it might be possible to detect compound concentrations less than the MDL; conversely, in complex samples, it might not be possible to detect compounds at concentrations greater than the MDL.

Recovery at different concentrations: For each sample matrix, samples were grouped by concentration and compared using the nonparametric Kruskal-Wallis test (reagent water) or Mann-Whitney test (ground water or surface water) to examine the null hypothesis that the mean recoveries were equal in each concentration (Miller and Miller, 1988). The *F*-test was used to compare the variance of recovery in each concentration to examine the null hypothesis that the precision was different in the two concentrations (Miller and Miller, 1988).

In reagent-water samples, mean recoveries were comparable at 1.0 µg/L (table 4), 0.1 µg/L (table 3), or 0.01 µg/L (table 9) for most compounds. For some compounds (Malathion, Parathion-methyl and pronamide), the mean recoveries were significantly lower (p <0.05; Mann-Whitney test) in the 0.1-µg/L sample set compared to the 1.0-µg/L set. For other compounds (cyanazine, *p,p'*-DDE, dieldrin, 2,6-diethylaniline, metribuzin, molinate, naproamide, prometon, propargite, and simazine), the mean recoveries were significantly higher (p <0.05; Mann-Whitney test) in the 0.1-µg/L sample set compared to the 1.0-µg/L set. These differences were relatively small (4 to 15 percent) and might also be the result of variation in instrument performance because each sample set was analyzed at different time periods. Similarly, in the 0.01-µg/L sample set (table 9), mean recoveries of some compounds (2,6-diethylaniline, chlorpyrifos, dacthal, EPTC, linuron, molinate, propachlor, prometon, propargite, Terbufos) were significantly greater (p <0.05; Kruskal-Wallis test) than in the 0.1- and 1.0-µg/L sample sets (tables 3 and 4). However, this 0.01-µg/L sample set was prepared from a different primary fortification solution than that for the 0.1- and 1.0-µg/L samples, so these differences might be the result of differences in the solution mixtures, as well as sample preparation and instrument calibration.

The average recovery and precision of all compounds in tables 3 and 4 were combined to calculate average recovery and precision in reagent water. The average short-term, single-operator precision in reagent water at the 0.1- and 1.0-µg/L level is 7 percent, and the average recovery is 73 percent. From table 9, the average precision of all compounds in reagent water at 0.01 µg/L is 8 percent, and the average recovery is 83 percent.

In the Denver Federal Center Well 15 ground-water samples, mean recoveries were comparable at 0.1-µg/L (table 7) and 1.0-µg/L (table 8) concentration levels for most compounds. As in the case of reagent water, mean recoveries of prometon and simazine were significantly higher (p <0.05; Mann-Whitney test) in the 0.1-µg/L sample set compared to the 1.0-µg/L sample set. A few additional compounds (disulfoton, α-HCH, phorate, tebuthiuron, Terbufos) had significantly higher recoveries (p <0.05; Mann-Whitney test) in the 0.1-µg/L sample set compared to the 1.0-µg/L sample set.

In surface-water samples from South Platte River, mean recoveries were comparable at 0.1 µg/L (table 5) and 1.0 µg/L (table 6) concentration levels for most compounds. As in the case of reagent-water and ground-water samples, mean recovery of prometon was significantly higher (p < 0.05; Mann-Whitney test) in the 0.1-µg/L sample set compared to the 1.0-µg/L sample set. Other compounds (alachlor, chlorpyrifos, disulfoton, α-HCH, ethoprop, Linuron, Malathion, metribuzin, Parathion-methyl, phorate) had significantly higher recoveries (p < 0.05; Mann-Whitney test) in the 0.1-µg/L sample set compared to the 1.0-µg/L sample set. In addition, the relative

standard deviations of some compounds (ethoprop, pronamide, prometon, chlorpyrifos, Diazinon) in the 0.1-µg/L sample set (table 5) were significantly higher ($p < 0.05$; *F*-test for comparison of variance) (10 to 22 percent) than in the reagent-water sample set (2 to 5 percent). Pronamide and Diazinon were among those compounds corrected for background concentration in samples from South Platte River.

Recovery in different matrices: The mean recovery of most compounds was higher in the reagent-water sample sets (tables 3, 4, and 9) compared to samples of surface water (tables 5 and 6) or ground water (tables 7 and 8). Pronamide had significantly higher recoveries ($p < 0.05$; Mann-Whitney test) (98 and 100 percent) in the Denver Federal Center Well 15 ground-water sample sets compared to reagent water (76 and 84 percent). In surface-water samples from South Platte River, mean recoveries of ethoprop and the dinitroaniline class of herbicides (benfluralin, ethafluralin, pendemethilin, trifluralin) were significantly higher ($p < 0.05$; Mann-Whitney test) (62 to 68 percent) than in reagent-water samples (46 to 54 percent).

Qualification or elimination of some compounds: A few compounds produced poor performance in all matrices and all concentrations. Dimethoate demonstrated small and variable recovery (7 to 25 percent) in all sample-matrix types as a result of breakthrough on the SPE columns. Breakthrough of Dimethoate in 10-L water samples using 10-g C-18 SPE columns was observed by Foreman and Foster (1991). This compound has the highest water solubility (20,000 mg/L) of the compounds tested, and apparently is not well retained by the C-18 phase. Breakthrough is a function of the volume of sample processed. Because the volume of sample processed is variable, the precision of this compound tends to be unacceptably high and variable. As a result of this poor performance, Dimethoate was deleted from the method in November 1994.

Desethylatrazine also demonstrated small recovery (9 to 19 percent) in all sample-matrix types because of poor retention on C-18 phase at 1-L sample volumes. However, because of the national importance of this metabolite, the compound was not deleted from the method, but the result is qualified by reporting an "E" code.

Carbofuran, Carbaryl, terbacil, and azimphos-methyl demonstrated variable performance because of problems in the GC/MS procedure, either as a result of injector or coelution and integration problems. These compounds are reported with an "E" code to qualify the result and caution the user that concentrations are estimated and need to be evaluated carefully because of variable performance. Carbofuran and Carbaryl, in particular, are subject to variable performance because of contamination of injection liners. Early method-performance evaluation (tables 3-8) was studied using Bond-Elut SPE columns that resulted in a white precipitate after elution from the SPE

column which contaminated the injection liner. Changing to Isolute SPE columns largely eliminated the precipitate and resulted in improved performance of carbofuran and Carbaryl (compared to results listed in tables 3-8). Despite the improvement in performance with the Isolute columns, these compounds are reported with an "E" code because of the potential for variable performance.

Estimated holding time: The estimated holding time of samples after extraction of the SPE column and storage at room temperature was estimated using a mathematically defined procedure (ASTM Procedure D-4841-88) (American Society for Testing and Materials, 1993). The maximum holding time is defined as the 90-percent lower confidence limit of a specified critical time. The critical time is defined as the time that a change in 10 percent of the compound concentration from day zero occurred and when precision of the method allowed that 10-percent change to be a statistically significant difference at the 90-percent confidence level.

The relative standard deviation of analysis of samples fortified at 1.0 µg/L (table 4) was used to estimate the number of samples needed to evaluate a significant change in concentration over time. The number of replicates (table 10) was calculated according to the following equation:

$$n = \left(\frac{t \times RSD}{D} \right)^2 \qquad (8)$$

where n = number of replicates;
t = Student's t-value, 3.707, based on seven replicates used in table 4;
RSD = relative standard deviation (table 4); and
D = 15 percent, maximum variation from mean to be tolerated.

For most compounds, n was less than 3 (table 10), so this value was selected for the holding-time study.

Reagent-water samples were fortified at 1.0 µg/L, extracted on day zero, and stored at room temperature. Triplicate samples were eluted from the SPE columns at discrete (3, 12, 14, and 28 days) time intervals over 28 days. All samples were analyzed in one batch at the end of the experiment. Table 10 lists the tolerable variation d, calculated from the following formula:

Table 10.--*Summary of statistical data used to determine estimated holding time of compounds on solid-phase-extraction columns held at 25 degrees Celsius*

[Reagent water samples were fortified at 1.0 µg/L, and triplicate samples were analyzed on days 3, 12, 14, and 28. *n*, number of replicates; *d*, determination; µg/L, micrograms per liter; conc., concentration; r^2, regression coefficient; --, estimated holding time could not be determined because compound did not decrease in concentration over 28-day test period; E code, estimated value]

Compound	Calculated holding time replicates (*n*)	Tolerable variation (*d*) (99 percent) (µg/L)	Extrapolated day zero conc. (µg/L)	Slope coefficient	Intercept (*d*)	Regression coefficient (r^2)	Estimated holding time (days)
Alachlor	1	0.084	1.2	-0.00195	1.083	0.07	43
Atrazine	2	.098	1.1	-.00364	.984	.15	27
Benfluralin	3	.071	.6	.00197	.541	.22	--
Butylate	1	.075	.9	-.00035	.865	.006	213
Chlorpyrifos	3	.113	1.0	-.00321	.884	.12	35
Cyanazine	2	.102	1.0	-.00792	.936	.58	13
Dacthal	2	.099	1.2	-.0027	1.090	.08	37
DDE, *p,p'*-	11	.105	.4	.01294	.283	.51	--
Diazinon	2	.087	1.0	-.01229	.952	.68	7
Dieldrin	2	.065	.9	.00717	.856	.45	--
Diethylanaline, 2,6-	2	.082	.9	-.00692	.810	.43	12
Disulfoton	1	.074	1.1	-.00694	1.055	.60	11
EPTC	1	.076	1.0	-.00039	.907	.01	194
Ethalfluralin	3	.074	.7	.00102	.620	.02	--
Ethoprop	1	.059	1.2	-.00255	1.103	.13	23
Fonofos	1	.070	1.0	-.00284	.975	.17	25
HCH, *alpha*-	1	.065	1.1	-.00241	1.030	.09	27
HCH, *gamma*-	1	.068	1.1	-.00267	1.027	.13	25
Linuron	3	.194	.4	.00111	.253	.04	--
Malathion	1	.100	1.1	-.00024	.992	.001	418
Metolachlor	2	.095	1.1	-.00265	1.039	.14	36
Metribuzin	2	.039	.4	-.00199	.395	.17	20
Molinate	1	.058	1.0	-.00205	.930	.20	28
Napropamide	1	.058	1.0	.00574	.971	.37	--
Parathion	2	.119	1.0	-.00145	.876	.04	82
Parathion-methyl	2	.112	1.0	-.00259	.866	.18	43
Pebulate	1	.068	1.0	-.00095	.899	.05	71
Pendimethalin	3	.077	.7	.00697	.641	.49	--
Permethrin, *cis*-	21	.136	.2	.00749	.110	.39	--
Phorate	1	.059	1.1	-.00621	1.011	.48	10
Prometon	3	.099	.7	-.00327	.641	.17	30
Pronamide	1	.089	1.1	-.00661	1.016	.30	13
Propachlor	1	.059	1.0	-.00383	.959	.44	15
Propanil	2	.104	1.2	-.00232	1.087	.23	45
Propargite	6	.107	.6	-.00844	.524	.46	13
Simazine	2	.070	.7	-.00293	.710	.24	24
Tebuthiuron	2	.110	1.0	-.00363	.655	.24	109
Terbufos	1	.071	1.0	-.00576	.916	.60	12
Thiobencarb	2	.100	1.1	-.00177	1.011	.04	56

Table 10.--*Summary of statistical data used to determine estimated holding time of compounds on solid-phase-extraction columns held at 25 degrees Celsius*---Continued

Compound	Calculated holding time replicates (*n*)	Tolerable variation (*d*) (99 percent) (µg/L)	Extrapolated day zero conc. (µg/L)	Slope coefficient	Intercept (*d*)	Regression coefficient (r^2)	Estimated holding time (days)
Triallate	2	0.081	1.0	-0.0022	0.923	0.11	37
Trifluralin	3	.071	.6	-.00137	.568	.15	9
Pesticides having poor performance and reported with an E code							
Atrazine, desethyl-	2	0.012	0.1	-0.00006	0.093	0.002	204
Azimphos-methyl	2	.108	.7	-.00548	.600	.36	20
Carbaryl	6	.437	.7	-.00983	.219	.32	44
Carbofuran	2	.141	.6	-.00856	.469	.38	16
Terbacil	2	.069	.6	-.00798	.511	.64	9
Pesticide deleted from method in November 1994							
Dimethoate	7	0.011	0.1	-0.00121	0.080	0.57	9
Surrogates							
HCH-d_6, *alpha*-	1	0.090	1.1	-0.00132	0.965	0.03	68
Diazinon-d_{10}	2	.124	1.0	-.01247	.873	.76	10
Terbuthylazine	2	.128	1.1	-.00239	.993	.07	54

$$d = \pm \frac{t \cdot s}{\sqrt{n}} \qquad (9)$$

where d = range of tolerable variation from initial concentration;
t = Student's *t*-value, 3.707, based on seven replicates used in precision study;
s = standard deviation (table 4); and
n = 3, number of replicates.

Linear curves were fit to the data and the day-zero intercept was calculated from the regression line. The estimated *d* value, in micrograms per liter, then was subtracted from the day-zero value to give the lower tolerable range of variation from the day-zero concentration. The intercept of the linear fit of the concentration in relation to the time line with the lower tolerable range concentration gives the estimated holding time. Diazinon, terbacil, Dimethoate, phorate, Diazinon-d_{10}, and trifluralin had estimated

holding times of 10 days or less (table 10). The shortest is Diazinon at 7 days, which is the maximum allowable holding time of the SPE columns after extraction for the method.

Automation--The method is ideally suited for automation using laboratory systems to prepare samples. The method, with minor modifications, has been successfully used with an AutoTrace SPE Workstation. An example of the procedure and parameter set-up used with the AutoTrace SPE Workstation is shown in Supplement A.

On-site extraction--The method also can be used with an optional on-site extraction procedure, which allows samples to be collected and processed at remote locations. This procedure reduces potential problems of exceeding the estimated pre-extraction holding-time limit of 4 days and avoids complications and expense of overnight shipping of samples to the laboratory.

CONCLUSIONS

From the data presented in this report, SPE and determination by GC/MS is shown to be a sensitive and reliable method for the determination of low concentrations of a broad range of pesticides in water samples. This report presents a method for routine analysis of 41 pesticides and metabolites in natural-water samples. Method detection limits range from 0.001 to 0.018 µg/L. Average short-term single-operator precision in reagent-water samples is 7 percent at the 0.1- and 1.0-µg/L levels and 8 percent at the 0.01-µg/L level. Mean recoveries in reagent-water samples are 73 percent at the 0.1- and 1.0-µg/L levels and 83 percent at the 0.01-µg/L level.

Because of GC or SPE problems, five compounds (desethylatrazine, azimphos-methyl, Carbaryl, carbofuran, and terbacil) demonstrated variable performance and are reported as estimated values. One compound, Dimethoate, was deleted from the method because of variable recovery by SPE.

REFERENCES CITED

American Society for Testing and Materials, 1992, Annual book of ASTM standards, Section 11, Water: Philadelphia, American Society for Testing and Materials, v. 11.01, p. 8-13.

_____1993, Annual book of ASTM standards, Section 11, Water: Philadelphia, American Society for Testing and Materials, v. 11.01, p. 31-44.

Bagnati, R., Benfenati, E., Davoli, E., and Fanelli, R., 1988, Screening of 21 pesticides in water by a single extraction with C-18 silica bonded phase columns and HRGC-MS: Chemosphere, v. 17, no. 1, p. 59-65.

Battista, Massimo, DiCorcia, Antonio, and Marchetti, Marcello, 1989, Extraction and isolation of triazine herbicides from water and vegetables by a double trap tandem system: Analytical Chemistry, v. 61, no. 9, p. 935-939.

Bellar, T.A., and Budde, W.L., 1988, Determination of nonvolatile organic compounds in aqueous environmental samples using liquid chromatography/mass spectrometry: Analytical Chemistry, v. 60, no. 19, p. 2076-2083.

Brooks, M.W., Jenkins, Jeffrey, Jimenez, Miguel, Quinn, Theresa, and Clark, J.M., 1989, Rapid method for the determination of alachlor, atrazine and metolachlor in groundwater by solid-phase extraction: Analyst, v. 114, p. 405-406.

DiCorcia, Antonio, Marchetti, Marcello, and Samperi, Roberto, 1989, Extraction and isolation of phenoxy acid herbicides in environmental waters using two adsorbants in one minicartridge: Analytical Chemistry, v. 61, no. 13, p. 1363-1367.

Edwards, T.K., and Glysson, G.D., 1988, Field methods for measurement of fluvial sediment: U.S. Geological Survey Open-File Report 86-531, 118 p.

Eichelberger, J.W., Behymer, T.D., and Budde, W.L., 1988, Method 525--Determination of organic compounds in drinking water by liquid-solid extraction and capillary GC/MS, *in* Methods for the determination of organic compounds in drinking water: Cincinnati, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, p. 325-356.

Fishman, M.J., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.

Foreman, W.T., and Foster, G.D., 1991, Isolation of multiple classes of pesticides from large-volume water samples using solid phase extraction cartridges, *in* Mallard, G.E., and Aronson, D.A., eds., U.S. Geological Survey toxic substances hydrology program--Proceedings of the technical meeting, Monterey, California, March 11-15, 1991: U.S. Geological Survey Water-Resources Investigations Report 91-4034, p. 530-533.

Gianessi, L.P., Peskin, H.M., and Puffer, C.A., 1986, A national data base of nonurban nonpoint source discharges and their effect on the Nation's water quality: Report prepared for the U.S. Environmental Protection Agency, Office of Standards and Regulations under Cooperative Agreement CR 811858-01-0, 14 p.

Gianessi, L.P., and Puffer, C.A., 1990 (revised 1991), Herbicide use in the United States: Washington, D.C., Resources for the Future, December 1990 (Revised April 1991), 128 p.

Gianessi, L.P., and Puffer, C.A., 1992a, Fungicide use in U.S. crop production: Washington, D.C., Resources for the Future, November 1992.

Gianessi, L.P., and Puffer, C.A., 1992b, Insecticide use in U.S. crop production: Washington, D.C., Resources for the Future, August 1992.

Hallberg, G.R., 1989, Pesticide pollution of groundwater in the humid United States: Agriculture, Ecosystems and Environment, v. 26, p. 299-367.

Hardy, M.A., Leahy, P.P., and Alley, W.M., 1989, Well installation and documentation and ground-water sampling protocols for the pilot National Water-Quality Assessment program: U.S. Geological Survey Open-File Report 89-396, 36 p.

Junk, G.A., and Richard, J.J., 1988, Organics in water--Solid-phase extraction on a small scale: Analytical Chemistry, v. 60, no. 5, p. 451-454.

Leistra, M., and Boesten, J.J.T.I., 1989, Pesticide contamination of groundwater in Western Europe: Agriculture, Ecosystems and Environment, v. 26, p. 369-389.

Miller, J.C., and Miller, J.N., 1988, Statistics for analytical chemistry (2d ed.): New York, Ellis Horwood Limited, 227 p.

Sandstrom, M.W., 1989, Field method for isolation of herbicides in surface and ground water using solid-phase extraction, *in* Pederson, G.L., and Smith, M.M., eds., U.S. Geological Survey second national symposium on water quality--Abstracts of the technical sessions, Orlando, Florida, November 12-17, 1989: U.S. Geological Survey Open-File Report 89-409, p. 82.

Sandstrom, M.W., in press, Filtration of water-sediment samples for determination of organic compounds: U.S. Geological Survey Water-Resources Investigations Report 95-4105.

Sandstrom, M.W., Wydoski, D.S., Schroeder, M.P., Zamboni, J.L., and Foreman, W.T., 1992, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of organonitrogen herbicides in water by solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 91-519, 26 p.

Thurman, E.M., Meyer, M.M., Pomes, M., Perry, C.E., and Schwab, A.P., 1990, Enzyme-linked immunosorbent assay compared with GC/MS for the determination of herbicides in water: Analytical Chemistry, v. 62, no. 18, p. 2043-2048.

Timme, P.J., 1994, National Water Quality Laboratory 1994 services catalog: U.S. Geological Survey Open-File Report 94-304, 103 p.

Ward, J.R., and Harr, C.A., eds., 1990, Methods for collection and processing of surface-water and bed-material samples for physical and chemical analyses: U.S. Geological Survey Open-File Report 90-140, 71 p.

Wershaw, R.L., Fishman, M.J., Grabbe, R.R., and Lowe, L.E., eds., 1987, Methods for the determination of organic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A3, 80 p.

U.S. Environmental Protection Agency, 1992, Guidelines establishing test procedures for the analysis of pollutants (App. B, Part 136, Definition and procedures for the determination of the method detection limit): U.S. Code of Federal Regulations, Title 40, revised as of July 1, 1992, p. 565-567.

Supplement A--Automated Solid-Phase Extraction Procedure Using AutoTrace Workstation

Zymark AutoTrace Extraction Workstation 1.20

[mL, milliliter]

AutoTrace Extraction Procedure: 2001 CONDITIONING/EXTRACTION 9/8/94
Estimated time for samples : 57.8 minutes
Date : 8 Sep 94
Step 1: Process 6 samples using the following procedure:
Step 2: Condition column with 3 mL of METHANOL into SOLVENT WASTE
Step 3: Condition column with 6 mL of WATER into SOLVENT WASTE
Step 4: Load 1,000 mL of sample onto column
Step 5: Dry column with gas for 4 minutes
Step 6: Pause and alert operator, resume when CONTINUE is pressed
Step 7: Clean each sample path with 50 mL into SOLVENT WASTE
Step 8: Clean each sample path with 50 mL into SOLVENT WASTE
Step 9: Clean each sample path with 100 mL into AQUEOUS WASTE
Step 10: Dry column with gas for 0.1 minute
Step 11: END

Setup Parameters

[mL/min, milliliters per minute; mL, milliliter]

AutoTrace Extraction Workstation

FLOW RATES (mL/min)		SOLID-PHASE EXTRACTION PARAMETERS	
Condition flow:	25	Push delay:	2 seconds
Load flow:	25	Air factor:	0.5
Rinse flow:	25	Autowash volume:	0.00 mL
Elute flow:	5		
Condition air push:	25	WORKSTATION PARAMETERS	
Rinse air push:	25	Maximum elution volume:	12.0 mL
Elute air push:	5	Exhaust fan on:	Y Y=Yes N=No
		Beeper on:	N Y=Yes N=No

Name Solvents

Solvent 1 : Water
Solvent 2 : Methanol
Solvent 3 : Solvent 3
Solvent 4 : Solvent 4
Solvent 5 : Solvent 5

Supplement B--On-site Solid-Phase Extraction Procedure

Solid-Phase Extraction, GC/MS Analysis, Filtered Water Schedule 2010

Instructions for On-Site Processing Using Solid-Phase Extraction (SPE)

1. Gather the equipment and supplies needed for on-site SPE listed in table 11.

2. Record the precleaned SPE column type, lot number, and weight on the field form. Prepare the SPE column by conditioning with about 2 mL of methanol, followed by about 2 mL of water to remove excess methanol. Allow the methanol and water to flow by gravity through the column. AT NO TIME SHOULD THE COLUMN GO DRY ONCE CONDITIONING HAS STARTED (If it does, add methanol then water to recondition again). Maintain the water in the column bed by replacing the water that drains through, or by using an on-off valve to stop all water from draining out of the column.

3. Tare the weight of the amber glass 1-L sample bottle. Collect, split, and filter samples using appropriate procedures (Sandstrom, 1995). Collect about 1 L of the sample in the 1-L sample bottle (do not completely fill the bottle; leave about a 2-cm headspace to add conditioner and surrogate).

4. Weigh and record the amount of sample collected. Add about 10 mL of the methanol using the bottle-top dispenser. Weigh and record the sample-plus-methanol weight.

5. Add the surrogate solution (1.25 ng/µL) contained in the 2-mL amber screw-cap vial (refer to Spike Kit Instruction Manual for more detailed information on use of micropipet). Use the 100-µL micropipet and a clean glass bore. Withdraw the solution into the glass bore, then put the tip into the sample bottle, below the surface of the sample (tip the bottle on the side if needed to reach below the surface with the tip of the micropipet), and press the plunger to deliver the surrogate to the sample. Withdraw the micropipet, remove and discard the glass bore, and rinse the orange-colored Teflon tip with methanol. Swirl the sample to mix. Detailed instructions on use of the micropipet are contained in the spike kit.

6. Obtain a plastic 1-L beaker for collecting the extracted water.

7. If necessary, adjust the pump flow rate to 20 to 25 mL/min using the cleaning solutions and graduated cylinder or beaker to measure volume.

8. Insert the inlet end of the Teflon-PFA tubing from the SPE pump into the sample bottle. Turn on the pump and allow the air to be rinsed from the Teflon tubing, then attach the Luer tip of the SPE column to the outlet end of the pump tubing. Invert the column to discard any conditioning water remaining in the SPE reservoir and begin collecting extracted water that passes through the column into the plastic beaker. Pump sample through the column at 20 to 25 mL/min. After sample has been pumped through column, turn off pump, disconnect SPE column, and record final weight of sample processed through the column.

9. Remove excess water from SPE column using a syringe to blow out water. Write sample ID on side of column, and store in 40-mL glass ampule. Store columns in cool place (between 4-25ºC).

CLEANING PROCEDURE

Clean all equipment after use by rinsing with a laboratory detergent (Liquinox solution, 0.2 percent), followed by rinses with about 30 mL of tap or distilled water to remove the detergent; finally, rinse with about 30 mL of methanol. Wrap all openings of cleaned material with aluminum foil.

Samples (and any materials added to samples) should contact only glass, Teflon, ceramic or stainless steel (or other metal).

QUALITY-ASSURANCE SAMPLES

Field equipment blank: Process a sample of pesticide-grade water (available from NWQL, through DENSUPL section) exactly as the samples. This includes sample bottles, compositing, splitting, and filtration equipment as well as the SPE system. Process the field-equipment blank at the start of sampling, and then after about every 10 to 15 samples. More frequent blanks are always helpful.

Field matrix spikes: Collect duplicate samples and add the 2.0-ng/µL spike solution to one sample. Use the 100-µL micropipet to add the spike solution, which is contained in a 2-mL glass vial, after about every 20 samples. Add the surrogate to every spiked sample.

FURTHER INFORMATION

Contact Frank Wiebe (EDOC - FWWIEBE; 303-467-8178), Mark Sandstrom (EDOC - SANDSTRO; 303-467-8086), or Steve Zaugg (EDOC - SDZAUGG; 303-467-8207) for additional information.

Table 11.--*Equipment and supplies required for broad spectrum pesticide analysis (Schedule 2010) by onsite solid-phase extraction*

[mm, millimeter; in., inch; mL, milliliter; SPE, solid-phase extraction; µL, microliter; g, gram; µm, micrometer; mg, milligram; L, liter; ng/µL, nanogram per microliter]

Item	Number per sample
Equipment	
Filter Unit, 147-mm diameter, aluminum, and FMI Model QB-1 CKC pump and 1/4-in. diameter convoluted Teflon tubing	1
Teflon squeeze bottle, 250 mL, for methanol	1
Valveless, piston-type metering pump for SPE; FMI Model RHB 0CKC	1
Fixed volume (100-µL) micropipet	1
Portable balance (1,200.0 g)	1
Filters, 147-mm diameter, 0.7-µm pore diameter, precleaned	1-5
Bottle-top dispenser, 1-5 mL, for methanol	1
Teflon squeeze bottle, 250 mL, for pesticide-grade water	1
Supplies	
SPE columns, Analytichem C-18, 500 mg, precleaned[1]	1
Sample bottles, 1-L, amber	1
Disposable glass bores, for 100-µL micropipet[1]	1
Surrogate mixture, 1.25 ng/µL, 2-mL vial[1]	1
Liquinox detergent, 0.2-percent solution, 4-L	1
B&J methanol, 4-L	1
B&J water, 4-L	1
Aluminum foil, roll	1
Gloves, disposable, nonpowdered, medium	1-5
Spike kit, including Instruction Manual[1]	1
Spike mixture, 1-10 ng/µL, 2-mL vial[1]	1

[1]Supplies obtained through NWQL DENSUPPL.

Solid-Phase Extraction, GC/MS Analysis, Filtered Water
Schedule 2010

Station ID or Unique Number: _____Station Name _____
Date: _____ Time _____ Collector: _____
Telephone Number of Collector: _____
Comments: _____

NWQL INFORMATION

SPE Cartridge Type: _____
Lot #: _____
Dry Wt.: _____ g

FIELD INFORMATION

Filter Sample 0.7-µm glass fiber filter Date filtered:_
SPE Cartridge Conditioning: Date of SPE procedure:_____
Methanol (2 mL): _____ mL
Organic-free water (2 mL): _____ mL
(DO NOT LET CARTRIDGE GO DRY ONCE CONDITIONING STARTED)

Sample Sample + bottle: _____ g
(-) bottle tare wt.: _____ g
= Sample wt.: _____ g
Add 1% methanol: _____ mL
Sample + bottle + MeOH: _____ g

Surrogate Solution ID: _____
Volume added: _____ µL

QA Samples - Spike Mixture
Solution ID: _____
Volume added: _____ µL

Sample through cartridge
Sample + plastic beaker: _____ g
plastic beaker: _____ g
Flow rate: Start time: _____ hr:min
Finish time: _____ hr:min

Remove excess water - Write station ID, date, time on cartridge - Store in 40-mL vial @ 4°C

NWQL INFORMATION

Lab ID: _____ Set #: _____ Date Received_____

Dry cartridge with CO_2: Date:
Pressure: _____ lb/in^2
Time: _____ min
SPE cartridge wt.: _____ g

SPE Elution Date:
add 1.8 mL HIP (3:1) _____ mL

Internal Standard (PAH-d_n mixture in toluene keeper)
Solution ID: _____
Volume added (100 µL): _____ µL

Evaporate solvent - nitrogen Date:
Pressure : _____ lb/in^2
Time: _____ min

Analysis - Instrument ID: _____ Date:

Comments: